# THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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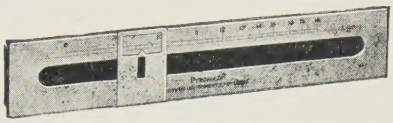

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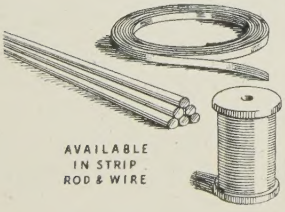

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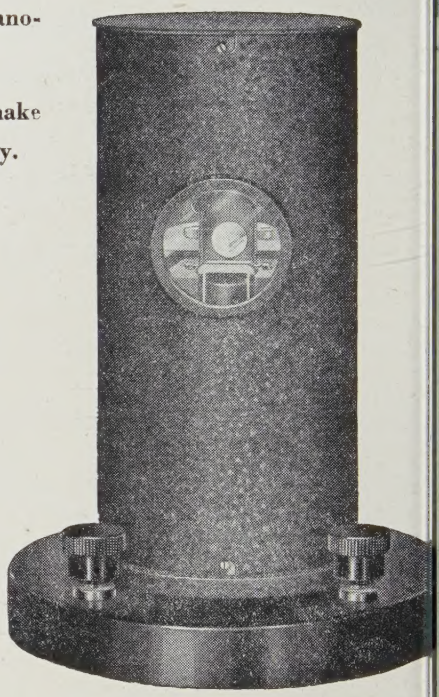

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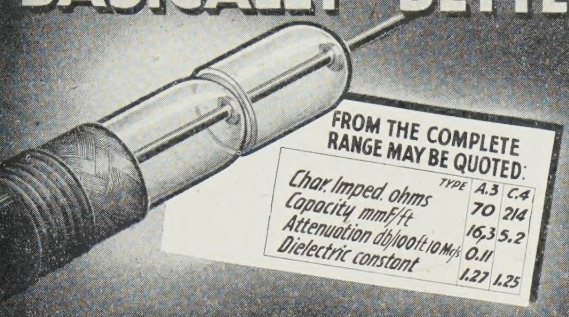
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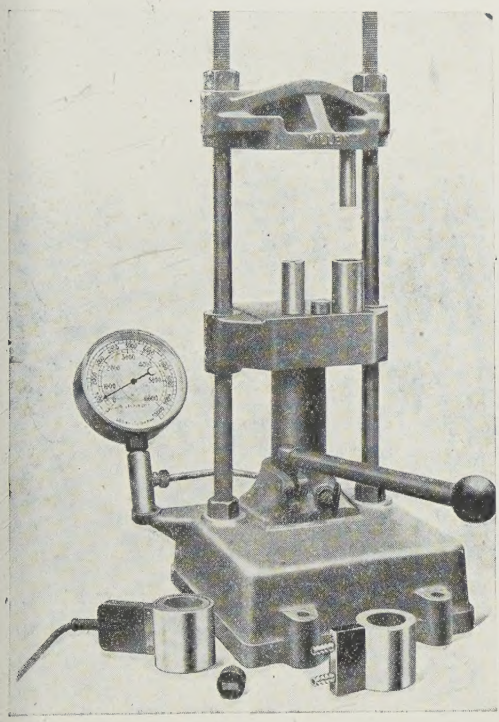

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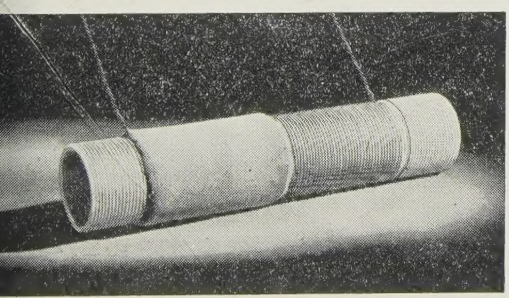

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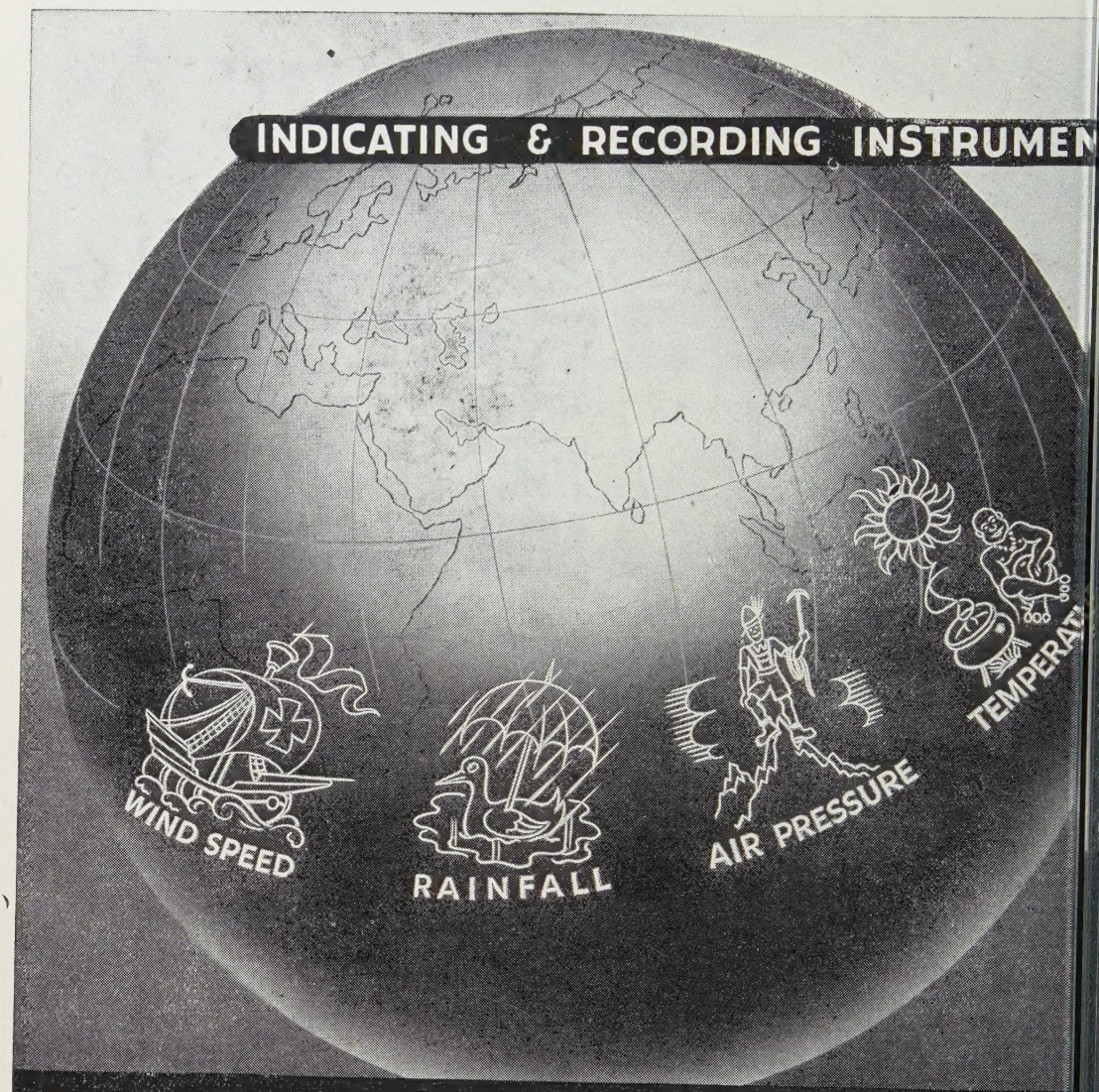


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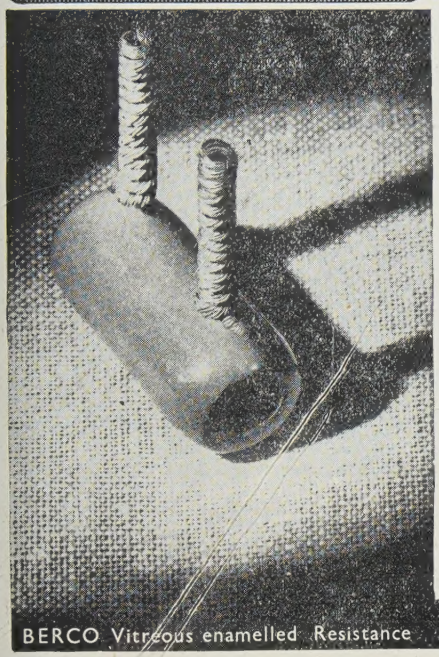

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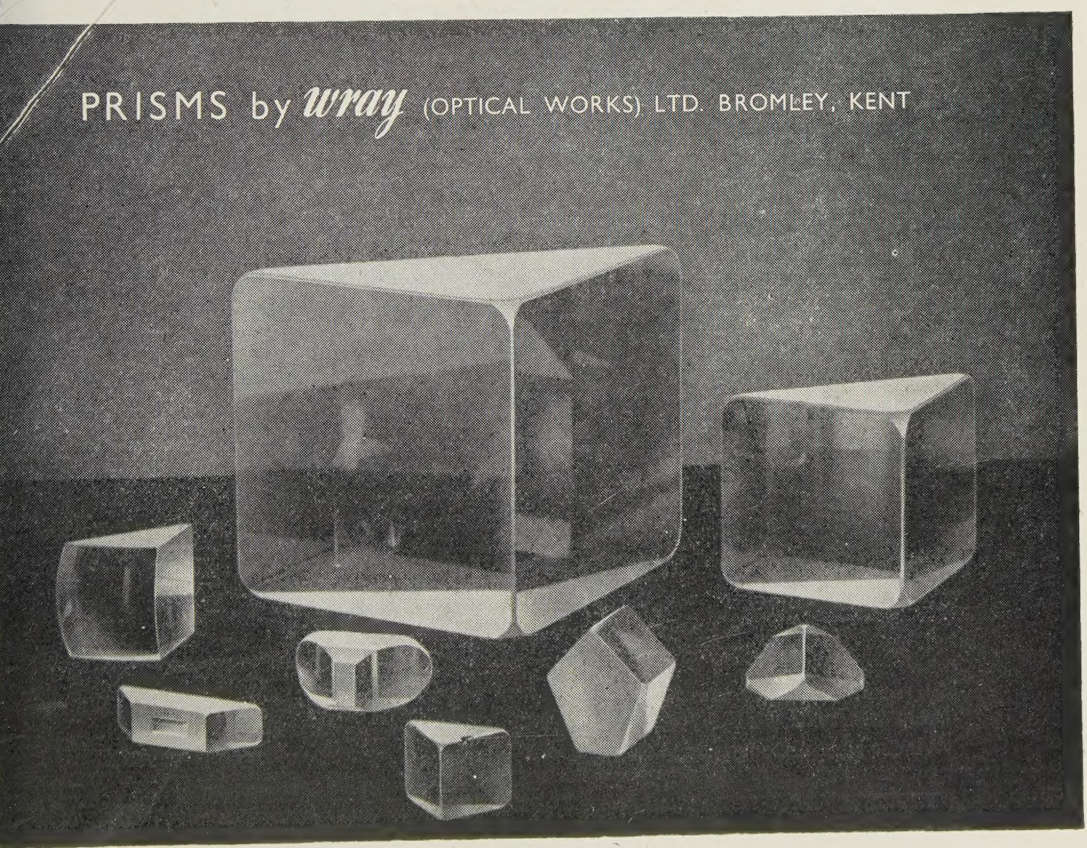

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THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 55, PART 5 1 September 1943 No. 311

# THE STATISTICAL LENGTH OF PARAFFIN MOLECULES

BY L. R. G. TRELOAR,
Welwyn Garden City

*MS. received* 20 *March* 1943

*ABSTRACT.* The relation derived theoretically by Kuhn to represent the probability of a given length (i.e. distance from end to end) for a thermally fluctuating paraffin molecule applies only when the number of chain atoms is large, and when the length is small compared with the length of the fully extended molecule. The present paper outlines methods by which the distribution of lengths over the whole range may be derived for molecules of any chain length. The results for paraffin chains of 3, 4, 5, 10, 20, 40 and 80 " links " are given. For the higher members of the series the departures from the Kuhn formula increase rapidly as the length approaches that of the extended chain. This result is of importance in the development of the kinetic theory of elasticity of rubber.

## § 1. THE SIGNIFICANCE OF THE PROBLEM

A NOTABLE advance in the theory of the elasticity of rubber has recently been made by Wall (1942), who has derived the stress-strain relations for an idealized network of long-chain molecules, representing the structure of vulcanized rubber, in elongation, unidirectional compression and shear. Wall's work rests on the fundamental basis of the kinetic theory of rubber elasticity worked out by Kuhn (1934, 36) and Guth and Mark (1934). This theory assumes, in accordance with the classical conceptions of organic chemistry, that in long thread-like molecules of the paraffin type, in which the chain atoms are linked by single valence bonds, there is free rotation of each bond about the adjacent bonds as axes. Thus, in figure 1, if $C_1C_2$ are the first two carbon atoms of a paraffin chain, the third atom, $C_3$, rotates * round the rim of the cone having $C_1C_2$ as axis, $C_4$ rotates round the rim of a second cone having $C_3$ as vertex, and so on. As a result, the molecule assumes a randomly-kinked, continually fluctuating form, in which the average length (i.e. distance between ends) is very much less than the outstretched length.† Assuming that in rubber-like materials the molecules are normally distributed about the most probable length, any deformation will cause a departure from this normal distribution, and on release of the deforming force the thermal motions will tend to restore the original (i.e. most probable) state. The elasticity is thus directly related to the statistical fluctuations of the molecule.

* The rotation is due to the thermal energy, and is, of course, not regular.

† X-ray work on the length of chain-like molecules in the crystalline state is concerned only with the outstretched length.

Both Kuhn and Guth and Mark have derived a formula for the probability of a given length in terms of the number of links in the chain, the length of each link, and the angle between adjacent bond directions. This formula has been used by Wall in his derivation of the stress-strain relations for a molecular network.

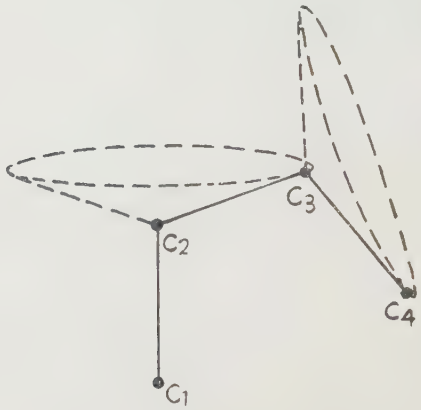


Figure 1. Rotations about bonds in paraffin molecule.

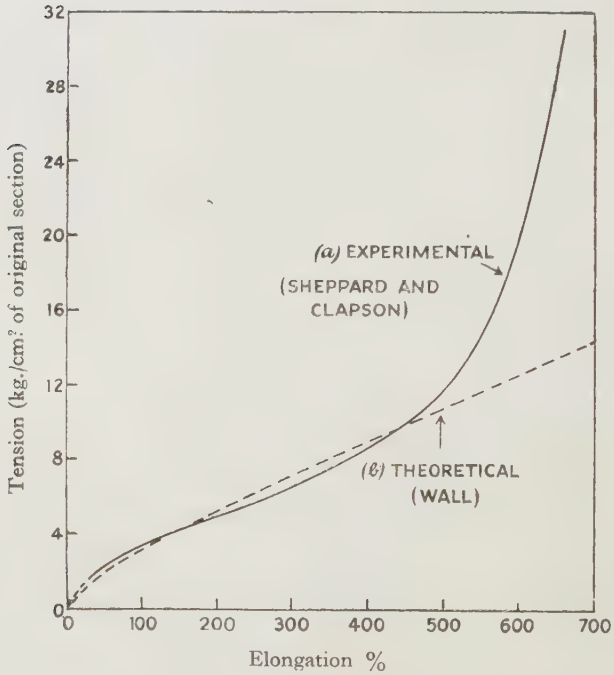


Figure 2. Comparison of theoretical and experimental stress-strain curves for rubber in elongation.

Owing to the assumptions on which it is based, the formula is applicable only when the number of links in the chain is large, and when its length is well below its outstretched length (chain length). It follows that Wall's equations cease to apply if the molecular extension is high, i.e. in the region where the deformation

of the rubber begins to approach the maximum possible. The practical effect of this limitation is apparent when the actual and theoretical stress-strain relations are compared. In figure 2, curve (*a*) is a typical stress-strain curve for vulcanized rubber in extension, taken from the data of Sheppard and Clapson (1932). Curve (*b*) represents Wall's relation. The characteristic upward bend of the experimental curve associated with the approach to full extension of the molecules is not reproduced by the theoretical relation. The first necessity in attempting to derive a more accurate quantitative theoretical relationship is, therefore, to modify Kuhn's distribution formula so as to take account of molecular lengths comparable with the chain length. In the following pages, a semi-graphical method by which this may be done is described and applied to the case of paraffin chains containing up to 80 links. Data are also given for short chains, which, though not required for the theory of elasticity, may be of interest in connection with other physical and chemical problems.

## § 2. THE STATISTICAL TREATMENT

In order to understand the significance of the methods to be considered in this paper, it is desirable first to examine very briefly the general method of approach adopted by Kuhn and others, and to consider the various approximations which have been introduced.

Kuhn considered a chain of $Z$ equal links, in which the direction of any given link is assumed in the first place to be independent of the directions of its neighbours. If we consider first the component of length, $x$, in a fixed direction, the probability that $x$ lies between $x$ and $x+dx$ is given by the approximate formula (Kuhn, 1934),

$$p_x dx = \frac{\beta}{\sqrt{\pi}} e^{-\beta^2 x^2} dx, \qquad \ldots\ldots(1)$$

where

$$\frac{1}{\beta^2} = \frac{2}{3} l_c^2 Z, \qquad \ldots\ldots(1\,a)$$

$l_c$ being the length of each link.

For the total length $r$ of the chain, considered to lie in any direction in space, the corresponding formula may be written (Kuhn, 1934)

$$p_r dr = \frac{\beta^3}{\pi^{3/2}} \cdot 4\pi r^2 e^{-\beta^2 r^2} dr. \qquad \ldots\ldots(2)$$

These approximate formulae rest on the assumption that $Z$ is large, and that $r$ (or $x$) is small compared with $l_c Z$. It is on their basis that the theories of elasticity of Kuhn and of Wall have been developed.

Rayleigh (1919), in a very full discussion of the problem of "random flights" in one, two and three dimensions, has shown how the probability $p_r$ in equation (2) may be derived, by *accurate* analytical methods, for any values of $Z$ and $r$, and has worked out expressions for $p_r$ corresponding to $Z=6$. In general, no single formula is applicable over the whole range of $r$, but a different formula is obtained for each successive interval of $2l_c$. The labour involved in working out and applying this method for a large value of $Z$ (e.g. $Z=50$) would appear to be prohibitive.

Rayleigh has also derived a more workable *approximate* formula for $p_r$ when $Z$ is large. Unfortunately, however, this, though giving a better approximation than (2), ceases to be accurate when $r$ is greater than $l_c\sqrt{Z}$, and does not therefore cover a sufficient range of $r$ for the present purpose.

*The valence-angle problem.* Kuhn's method is not adaptable to the direct handling of the problem in which each link makes an angle $\alpha$ with its neighbours. An indirect solution is obtained by Kuhn, in which Eyring's formula for the root-mean-square length of a paraffin chain of $Z$ links is utilized to correct the parameter $\beta$ in equation (2). Eyring's formula (Eyring, 1932) depends on a process of summation of a series of vectors, and is exact. It gives, for the mean square length $\overline{r^2}$,

$$\overline{r^2} = l_c^2[Z + 2(Z-1)\cos\alpha + 2(Z-2)\cos^2\alpha + \ldots + 2\cos^{Z-1}\alpha]. \qquad \ldots\ldots(3)$$

If $Z$ is large this becomes

$$\overline{r^2} = l_c^2 Z \frac{1+\cos\alpha}{1-\cos\alpha}. \qquad \ldots\ldots(3\,a)$$

Hence by substituting for (1 *a*) the expression

$$\frac{1}{\beta^2} = \frac{2}{3} l_c^2 Z \frac{1+\cos\alpha}{1-\cos\alpha}, \qquad \ldots\ldots(1\,b)$$

Kuhn's formula (2) gives the correct value of $\overline{r^2}$. For the C—C bond the value of $\cos\alpha$ is $\frac{1}{3}$, and $\frac{1+\cos\alpha}{1-\cos\alpha} = 2{\cdot}0$. The effect of the valence angle is, therefore, to spread out the probability function (2) to $\sqrt{2}$ times its original width.

Like the approximations already considered, this approximate method of introducing the valence-angle condition is valid only for small values of $r$.

## § 3. THE GENERAL METHOD

The present method starts from the short chain and proceeds gradually to chains of increasing length. The distribution functions for 3-link, 4-link and 5-link paraffin chains are accurately derived, no approximations being introduced except those inherent in graphical integration, the degree of accuracy obtainable being limited only by the amount of labour expended in the graphical operations. The valence-angle effect is properly accounted for by the methods employed. The same degree of accuracy is not possible in the longer chains. The 10-link chain distribution is derived by considering the joining up of two 5-link chains, the directions of the two segments being considered independent (i.e. unaffected by valence-angle considerations). Though not strictly true, this assumption is very near to the truth, as will be evident later. Two 10-link distributions are then compounded to yield the 20-link distribution, in which case the neglect of residual directional effects will produce a still smaller error. The 40-link distribution is then derived by compounding two 20-link distributions, and the 80-link from two 40-links. The process may be repeated indefinitely.

In the presentation of the paper the aim will be to give a clear outline of the methods employed and the results obtained, with the minimum of mathematical detail. A fuller consideration of the mathematical details will be given in an appendix to the paper.

## § 4. THE 2-LINK CHAIN

In the following discussion the length of a link is taken as unity. For the paraffins, the valance angle is taken to be $109\frac{1}{2}^\circ$, so that $\cos\alpha = \frac{1}{3}$. The distance between the ends of the 2-link chain is constant, and is given by

$$r = 2\cos\alpha/2 = 1{\cdot}633.$$

## § 5. THE 3-LINK CHAIN

The method of handling the 3-link chain may be understood from figure 3. The links AB and BC are considered fixed, while the third link, CE, rotates about the axis BC. If P is the instantaneous position of E, and OP makes an angle $\theta$

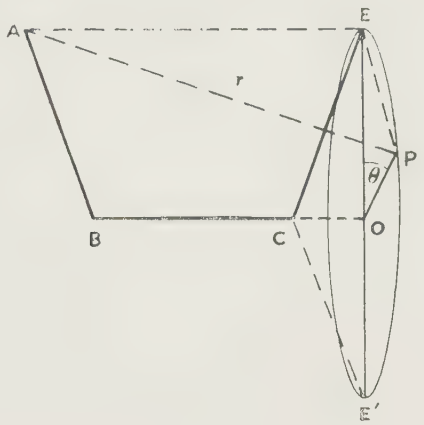


Figure 3. The 3-link chain.

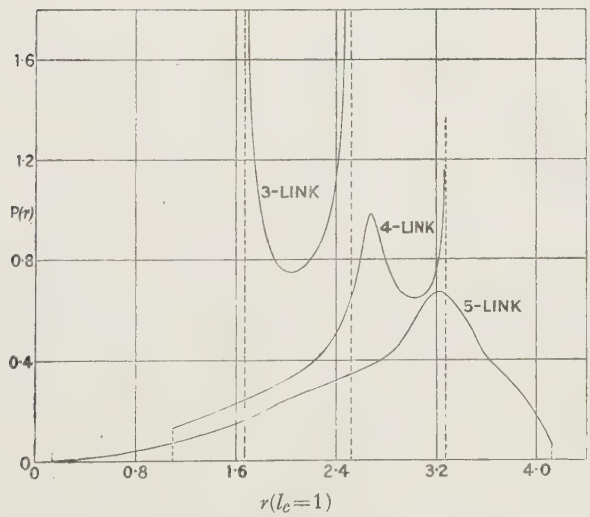


Figure 4. The distribution functions for paraffin chains of 3, 4 and 5 links.

with OE, the distance $r$ between the ends of the molecule may be defined in terms of fixed quantities and the variable angle $\theta$ (see Appendix, § 1). If $p(r)\Delta r$ is the probability that $r$ lies between $r$ and $r+\Delta r$, and $p_1(\theta)\Delta\theta$ the probability that $\theta$ lies between $\theta$ and $\theta+\Delta\theta$, we have, obviously,

$$p(r)\Delta r = p_1(\theta)\Delta\theta.$$

If all values of $\theta$ are equally probable, $p_1(\theta)$ is constant, and since $dr/d\theta$ is obtainable by a geometrical analysis, $p(r)$ may be determined. The result is

$$p(r) = \frac{9r}{8\pi\left[1-\left(2\frac{9}{16}-\frac{9}{16}r^2\right)^2\right]^{\frac{1}{2}}}. \qquad \ldots\ldots(4)$$

This function is plotted in figure 4. Though it tends to infinity at an upper and a lower limit of $r$, the probability over any finite interval $\Delta r$ is always finite.

## § 6. THE 4-LINK CHAIN

The argument by which the 4-link distribution is obtained is rather more involved. It is necessary first to establish a probability relation in the case of two links rotating about an axis. This preliminary problem may be understood by reference to figure 5. The link OB rotates about OX, making an angle $\alpha$

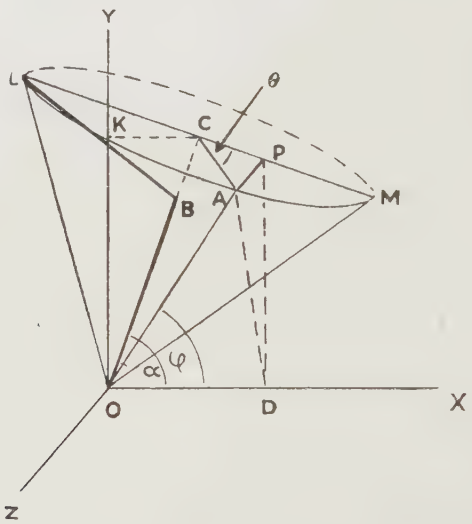


Figure 5. The $\phi$-distribution problem.

thereto, and the link BL rotates about OB. If A is the instantaneous position of L, it is required to find the probability $p(\phi)$ of a given angle $\phi$ between OA and OX, assuming all positions of the links to be equally probable. This may be found from geometrical considerations, by an argument of the same kind as that in the preceding paragraph (Appendix, § 2).

Returning now to the 4-link chain, the first two links AB and BC (figure 6) are assumed fixed, and the remaining two links are replaced by a line CE of fixed length, $(2\cos\alpha/2)$ making an angle $\phi$ with AB, the probability of a given value of $\phi$ being given by $p(\phi)$. If P is the instantaneous position of E, all positions of P round the circle are equally probable. The determination of the distribution function $p(r)$ for a fixed value of $\phi$ is, therefore, a problem of exactly the same kind as the 3-link problem considered in section 5, and the result is

$$\int_{r_0}^{r} p(r)dr = \frac{1}{\pi}\operatorname{arc\,cos}\left(\frac{5{\cdot}34+4{\cdot}36\cos\phi-r^2}{3{\cdot}08\sin\phi}\right). \qquad \ldots\ldots(5)$$

This represents the partial distribution of the $r$-values for a particular value of $\phi$. It is given in the integral form because the differential form is not always finite, and hence cannot conveniently be handled by graphical methods.

The $\phi$-distribution function may be divided up into a convenient number of elements, so that instead of a continuous function we have the probabilities $p_1$, $p_2$, $p_3$, .... associated with the angles $\phi_1$, $\phi_2$, $\phi_3$, .... The partial distribution function (5) is evaluated for each of these values of $\phi$, and multiplied by a factor representing the appropriate probability $p(\phi)$. These elementary distributions are plotted, and by addition of the curves the total distribution of $r$-values, $\int^r P(r)dr$, is obtained. From this the differential function $P(r)$, representing the probability of a given value of $r$, is readily derived.

In carrying out the calculation, the $\phi$-function was divided into 16 elements, separated by approximately 5° from each other. The plotting was simplified

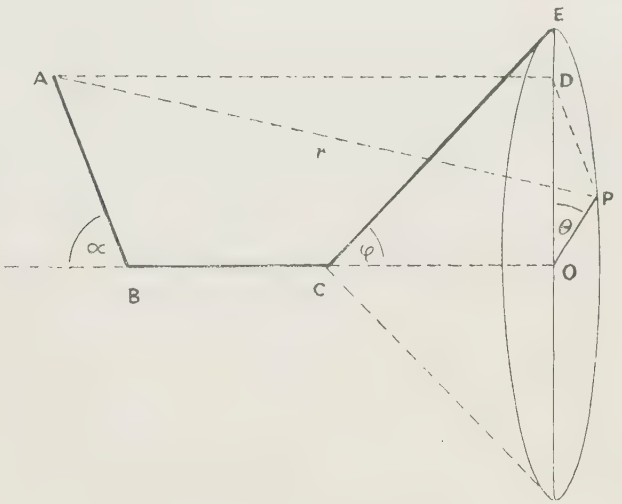


Figure 6. The 4-link chain.

by using $r^2$ as abscissa, in which case the curves corresponding to (5) reduce to cosine curves. The resultant $\int P(r)dr$ curve was transposed to the $r$-plot. The final differentiation involved comparatively large errors, amounting perhaps to 5 %, but such errors would not affect the important features of the final distribution curve (figure 4). The only exception is at the extreme upper end of the curve, where the graphical accuracy is not sufficient to establish whether or not $P(r)$ tends to infinity at the upper limit of $r$, $(r_m)$. Actually it may be shown independently (see Appendix, § 2) that $P(r)$ does become infinite at $r = r_m$.

## § 7. THE 5-LINK CHAIN

In dealing with the 5-link chain, the middle link BC (figure 7) is assumed fixed. The two links on one side are replaced by the line CE of length $2\cos\alpha/2$, making an angle $\phi$ with BC, and the remaining two links are replaced by the line AB of the same length, making an angle $\psi$ with BC. The angles $\phi$ and $\psi$ are

variable, and the probability to be associated with a given value of $\phi$ or $\psi$ is given by the function $p(\phi)$, referred to earlier as the $\phi$-distribution function.

For given values of $\phi$ and $\psi$, the elementary distribution of $r$-values corresponding to the rotation of CE about BC is given by an expression analogous to (5), i.e.,

$$\int_{r_0}^{r} p(r)dr = \frac{1}{\pi} \arccos\left[\frac{6{\cdot}34 + 3{\cdot}27(\cos\phi + \cos\psi) + 5{\cdot}34\cos\phi\cos\psi - r^2}{5{\cdot}34\sin\phi\sin\psi}\right]. \quad \ldots\ldots(6)$$

The $\phi$ and $\psi$ distributions are divided into elements represented by the probabilities $p_1(\phi)$, $p_2(\phi)\ldots$. and $p_1(\psi)$, $p_2(\psi)\ldots$. respectively. The various $\phi$-elements have to be combined with the $\psi$-elements in a random manner. Since the angles $\phi$ and $\psi$ are independent, the probability of a given $\phi$-element and a given $\psi$-element occurring together is $p(\phi).p(\psi)$, and the function (6) has

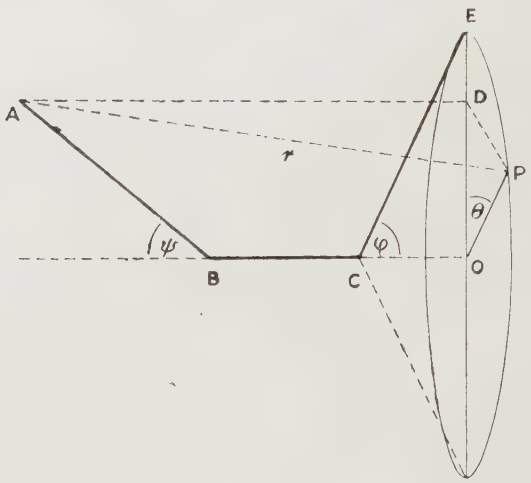


Figure 7. The 5-link chain.

therefore to be multiplied by this factor. The remaining operations are the same as for the 4-link chain.

In carrying out these operations, the $\phi$ and $\psi$ distributions were each divided into 9 elements, giving 81 combinations. Not all of these were different, and only 45 distribution curves had to be plotted. Addition of the curves and graphical differentiation yielded the result shown in figure 4.

## § 8. PROPERTIES OF THE SHORT-CHAIN DISTRIBUTION CURVES

The remarkable changes in type of distribution function in passing from the 3- to the 5-link chain are interesting in that they reveal the rapid trend towards the Kuhn type, or purely random form with increasing number of links in the chain, and the submergence of the special features relating to the geometry of the system. In this sense the 4-link chain is of particular interest. It shows a hump in the middle region, whilst retaining the asymptotic form at one extreme.

As a check on the numerical accuracy, the mean value of $r^2$ for each of the distribution curves may be compared with the value given by Eyring's formula (3). This comparison is made in table 1.

Table 1. Mean values of $r^2$.

| No. of links | Author | Eyring | Difference (%) |
|---|---|---|---|
| 4 | 6·53 | 6·518 | + 0·18 |
| 5 | 8·50 | 8·504 | − 0·05 |
| 10 | 17·0 | 18·50 | − 8·1 |
| 20 | 34·0 | 38·50 | −11·7 |
| 40 | 68·5 | 78·5 | −12·7 |
| 80 | 138·4 | 158·5 | −12·7 |

For the 4- and 5-link chains the agreement is within 0·2 %. This represents a reasonable degree of accuracy for the graphical methods employed.

## § 9. THE MULTI-LINK CHAINS

For the higher chain-lengths, the problem becomes too complex to be treated by the exact methods described for the 3-, 4- and 5-link chains. To proceed, it is assumed that two 5-link chains are joined entirely at random. Given the distribution function $p(r)$ for the 5-link chain, the problem is to determine the distribution function $P(r)$ for a 10-link chain formed by the random joining of two 5-link chains.

Considering first the joining of two links of lengths $r_1$ and $r_2$ respectively (figure 8), it is easy to derive an expression for the probability of a distance $r$

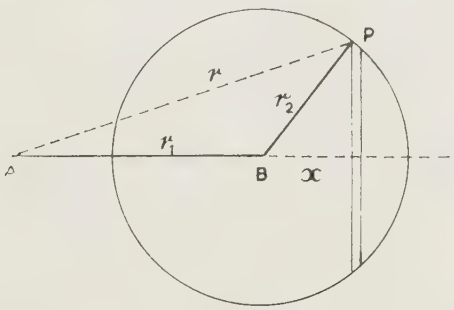


Figure 8. The joining of two links of different length at random.

between the ends of the 2-link chain, on the assumption that all angles between $r_1$ and $r_2$ are equally probable. The result is given by equation (13) (Appendix, § 4).

In applying this result to the joining of two 5-link chains, the method employed is essentially the same as that described in section 7 for dealing with the 5-link problem. The 5-link distribution function is divided into elements $p_1(r_1)$, $p_2(r_2)$, etc. Knowing the probability $p_1(r_1)$ that the first "link" of the 2-link chain has the length $r_1$ and the probability $p_2(r_2)$ that the second "link" has the length $r_2$, the probability of a first "link" of length $r_1$ joining a second "link" of length $r_2$ is $p_1(r_1) \cdot p_2(r_2)$, and the elementary distribution of

lengths resulting from the random combination of these two "links" is given by (13). Combination of the $r_1$s and $r_2$s in all possible ways, and addition of the elementary distributions thus derived, leads to the distribution function $P(r)$ for the 10-link chain.

The higher-membered chains were obtained in a similar way. The number

Table 2. High-$r$ portions of distribution functions

| 10-link | | 20-link | | 40-link | | 80-link | |
|---|---|---|---|---|---|---|---|
| $r$ | $\log_{10}P(r)$ | $r$ | $\log_{10}P(r)$ | $r$ | $\log_{10}P(r)$ | $r$ | $\log_{10}P(r)$ |
| 7·0 | $\bar{2}$·34 | 10·5 | $\bar{2}$·17 | 15·0 | $\bar{2}$·02 | 20·0 | $\bar{2}$·12 |
| 7·2 | $\bar{2}$·13 | 11·0 | $\bar{3}$·93 | 16·0 | $\bar{3}$·75 | 22·0 | $\bar{3}$·80 |
| 7·4 | $\bar{3}$·86 | 11·5 | $\bar{3}$·66 | 17·0 | $\bar{3}$·45 | 24·0 | $\bar{3}$·40 |
| 7·6 | $\bar{3}$·53 | 12·0 | $\bar{3}$·34 | 18·0 | $\bar{3}$·14 | 26·0 | $\bar{4}$·96 |
| 7·8 | $\bar{3}$·13 | 12·5 | $\bar{4}$·98 | 19·0 | $\bar{4}$·73 | 28·0 | $\bar{4}$·41 |
| 8·0 | $\bar{4}$·55 | 13·0 | $\bar{4}$·54 | 20·0 | $\bar{4}$·26 | 30·0 | $\bar{5}$·78 |
| 8·1 | $\bar{5}$·93 | 13·5 | $\bar{4}$·00 | 21·0 | $\bar{5}$·71 | 32·0 | $\bar{5}$·09 |
| 8·2 | $\bar{6}$·65 | 14·0 | $\bar{5}$·35 | 21·5 | $\bar{5}$·40 | 34·0 | $\bar{6}$·34 |
| 8·22 | $\bar{7}$·79 | 14·5 | $\bar{6}$·62 | 22·0 | $\bar{5}$·06 | 36·0 | $\bar{7}$·55 |
| 8·24 | $-\infty$ | 15·0 | $\bar{7}$·83 | 22·5 | $\bar{6}$·70 | 38·0 | $\bar{8}$·68 |
| | | 15·5 | $\bar{8}$·80 | 23·0 | $\bar{6}$·33 | 40·0 | $\bar{9}$·70 |
| | | 15·8 | $\bar{9}$·75 | 23·5 | $\bar{7}$·92 | 41·0 | $\bar{9}$·16 |
| | | 16·0 | $\bar{1}\bar{0}$·55 | 24·0 | $\bar{7}$·50 | 42·0 | $\bar{1}\bar{0}$·52 |
| | | 16·2 | $\bar{1}\bar{2}$·9 | 24·5 | $\bar{7}$·04 | 43·0 | $\bar{1}\bar{1}$·87 |
| | | 16·3 | $\bar{1}\bar{3}$·4 | 25·0 | $\bar{8}$·57 | 44·0 | $\bar{1}\bar{1}$·20 |
| | | 16·4 | $\bar{1}\bar{5}$·1 | 25·5 | $\bar{8}$·08 | 45·0 | $\bar{1}\bar{2}$·40 |
| | | 16·48 | $-\infty$ | 26·0 | $\bar{9}$·57 | 46·0 | $\bar{1}\bar{3}$·54 |
| | | | | 26·5 | $\bar{9}$·03 | 47·0 | $\bar{1}\bar{4}$·65 |
| | | | | 27·0 | $\bar{1}\bar{0}$·49 | 48·0 | $\bar{1}\bar{5}$·7 |
| | | | | 27·5 | $\bar{1}\bar{1}$·89 | 49·0 | $\bar{1}\bar{6}$·7 |
| | | | | 28·0 | $\bar{1}\bar{1}$·16 | 50·0 | $\bar{1}\bar{7}$·7 |
| | | | | 28·5 | $\bar{1}\bar{2}$·37 | 51·0 | $\bar{1}\bar{8}$·7 |
| | | | | 29·0 | $\bar{1}\bar{3}$·54 | 52·0 | $\bar{1}\bar{9}$·6 |
| | | | | 29·5 | $\bar{1}\bar{4}$·69 | 53·0 | $\bar{2}\bar{0}$·5 |
| | | | | 30·0 | $\bar{1}\bar{5}$·8 | 54·0 | $\bar{2}\bar{1}$·3 |
| | | | | 30·5 | $\bar{1}\bar{6}$·7 | 55·0 | $\bar{2}\bar{3}$·9 |
| | | | | 31·0 | $\bar{1}\bar{7}$·3 | 56·0 | $\bar{2}\bar{4}$·5 |
| | | | | 31·5 | $\bar{1}\bar{9}$·2 | 57·0 | $\bar{2}\bar{5}$·0 |
| | | | | 31·8 | $\bar{2}\bar{1}$·6 | 58·0 | $\bar{2}\bar{7}$·3 |
| | | | | 32·0 | $\bar{2}\bar{2}$·2 | 59·0 | $\bar{2}\bar{9}$·4 |
| | | | | 32·2 | $\bar{2}\bar{4}$·6 | 60·0 | $\bar{3}\bar{1}$·4 |
| | | | | 32·4 | $\bar{2}\bar{6}$·5 | 61·0 | $\bar{3}\bar{3}$·1 |
| | | | | 32·5 | $\bar{2}\bar{9}$·0 | 62·0 | $\bar{3}\bar{6}$·1 |
| | | | | 32·6 | $\bar{3}\bar{0}$·9 | 63·0 | $\bar{4}\bar{0}$·0 |
| | | | | 32·96 | $-\infty$ | 64·0 | $\bar{4}\bar{8}$·7 |
| | | | | | | 64·5 | $\bar{5}\bar{3}$·3 |
| | | | | | | 65·0 | $\bar{6}\bar{0}$·8 |
| | | | | | | 65·9 | $-\infty$ |

of elements chosen in dividing up $p(r)$ varied from 10 to 12. Certain devices were used to reduce the amount of labour involved. These are discussed in the Appendix.

It is not convenient to present the whole of the data for the multi-link chains in graphical form, because of the enormous range of $P(r)$. Consequently the results are given partly in graphical form (figure 9) and partly in tables (table 2).

The mean values of $r^2$ for the multi-link chains are given in table 1. The comparison with Eyring's values gives an indication of the error introduced by the neglect of the residual directional effect due to the valence angle, an effect which is bound to increase the average length of the resulting chain. The greatest directional effect occurs in the shortest chains. Thus, in joining two 5-link chains, the error introduced by the assumption of complete randomness

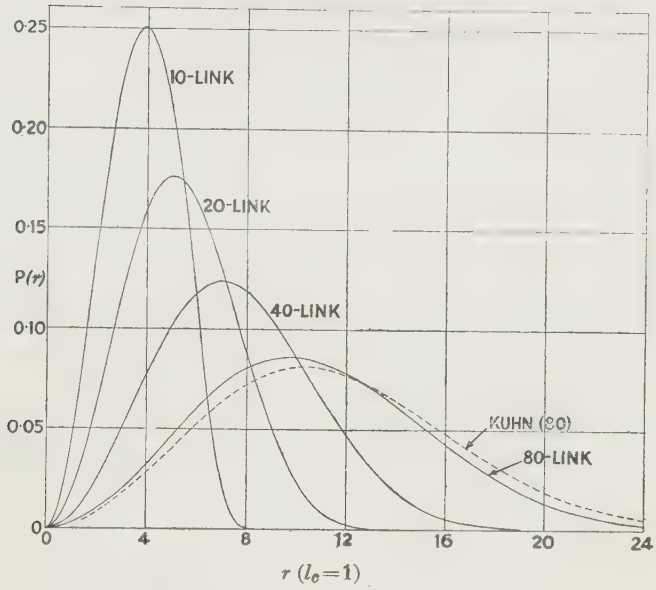


Figure 9. The distribution functions for multi-link chains.

is represented by an 8% reduction in $\overline{r^2}$; in the 20-link chain this is increased to ~12%, and in the 40-link to ~13%, whilst in the 80-link there is no further change, showing that the directional effect is no longer appreciable. These departures from the true values are not of sufficient magnitude to be considered important, though the approximation introduced may have an effect on the shape of the distribution curve, which might be significant in the immediate vicinity of the maximum length $r_m$.

## § 10. GENERAL TREND OF DISTRIBUTION CURVES

From figures 4 and 9 it is apparent that, in regard to that portion of the distribution curve visible on the scale chosen, there is a progressive tendency for the features corresponding to the special geometry of the chain structure to disappear with increase in the number of links. The higher-membered chains degenerate into the purely random type of distribution, as is seen by comparing the 80-link distribution with that derived from Kuhn's formula (2), shown in broken line (figure 9). It is rather interesting to see how this gradual change takes place, and the agreement in form between the higher-membered chain distributions and the Kuhn distribution provides a useful check on the correctness of the methods employed. There is a slight quantitative discrepancy between the 80-link distribution and the 80-link Kuhn distribution (figure 9), due to the neglect of certain directional effects discussed in the preceding section. The

effect of this is that the nearest approximation to the 80-link distribution is given by the Kuhn formula for a 71-link chain.

It is *not* to be concluded from these comparisons that there are no significant differences between the actual distribution and that given by the Kuhn formula. On the contrary, departures from the Kuhn formula become increasingly serious with increase in $Z$ over the region in which $r$ is beyond the range represented

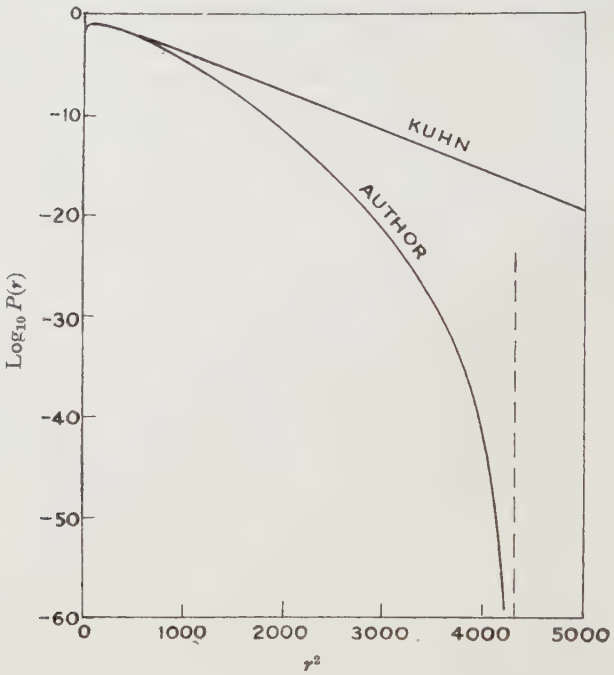


Figure 10. Comparison of distribution function for 80-link chain with that given by Kuhn's formula.

in figure 9, as will be seen if the data in table 2 are compared with the probabilities derived from formula (2). One example only of this departure is represented graphically (figure 10), in order to illustrate the magnitude of the difference. In this figure $\log_{10}P(r)$ is plotted against $r^2$. On this plot the Kuhn relation is almost linear when $r$ is large. The actual $P(r)$ begins to fall below the Kuhn curve at $r=25$, whilst at $r=64$ the difference amounts to a factor of $\sim 10^{30}$.

## § 11. SIGNIFICANCE OF RESULTS IN THEORY OF ELASTICITY

The discrepancy between the experimental stress-strain curve for rubber and the theoretical relation derived by Wall on the basis of Kuhn's distribution formula has been referred to in section 1. Though it is not intended in this paper to consider the detailed application of the more accurate distribution functions to the elastic network, it is worth while indicating in a general way the kind of effect which would result from such an application.

The entropy of a system of molecules in the extended state is directly related to the logarithm of the probability that they shall have the particular distribution of lengths corresponding to that state. According to Wall's analysis, if the

network is extended by the relative amount $\alpha$, the entropy change $S$ due to the extension, based on the Kuhn formula, is

$$S = -\tfrac{1}{2}\boldsymbol{Nk}(\alpha^2 + 2/\alpha - 3).$$

For large values of $\alpha$, the entropy is thus a linear function of $\alpha^2$, just as in Kuhn's formula $\log P(r)$ is a linear function of $r^2$, and the tension, which involves the derivative of $S$ with respect to $\alpha$, is proportional to $\alpha$, i.e. the stress-strain relation is approximately linear. But if $\log P(r)$ falls away much more rapidly with increasing $r^2$ (as in figure 10) the change in entropy on extension will follow a very similar course, and the tension curve, instead of being linear, will show a strong upward curvature, which will be related inversely to the curvature of the function $P(r)$. This therefore accounts qualitatively for the familiar upward bend of the stress-strain curve of rubber. The kinetic theory thus gives a natural explanation of the general shape of the stress-strain curve. Firstly, there is the upward convexity at low elongations, satisfactorily represented by Wall's relation, and secondly, the upward concavity at high extensions, which appears only when the more accurate distribution functions are employed.

### § 12. APPLICATION TO RUBBER

The foregoing treatment leaves out of account the volume occupied by the atoms, and the fact that one portion of the chain cannot pass through another portion. These effects will operate to increase the mean value of $r$, and are probably mainly responsible for the rather large discrepancy between the actual and theoretical extensibility of rubber (Treloar, 1943).

The treatment has been applied to the paraffin chain because this is a simpler system than the rubber (poly-isoprene) chain, and also because of the many theoretical works which have dealt with this system. There would be no difficulty in applying the same methods to the rubber chain, though on account of its more unsymmetrical form, the same degree of accuracy might not be obtainable. Moreover, the extra bulk of the methyl side-group and the rigidity of the C—C = C—C structure would probably result in a larger departure of the theoretical postulates from the actual physical conditions.

## APPENDIX

### § 1. THE 3-LINK CHAIN

From figure 3, we have by geometry, since $\angle \mathrm{AEP} = 90°$,

$$r^2 = \mathrm{AP}^2 = \mathrm{AE}^2 + 2\mathrm{OP}^2(1 - \cos\theta),$$

which, on insertion of numerical values (taking $\mathrm{BC} = 1$), gives

$$r^2 = \left(\frac{5}{3}\right)^2 + 2 \times \frac{8}{9}(1 - \cos\theta)$$

or

$$\cos\theta = 2\frac{9}{16} - \frac{9}{16}r^2. \qquad \ldots\ldots(7)$$

Since the system is symmetrical about the diameter EE′, it is sufficient to consider rotation through one semicircle only. If all values of $\theta$ are equally

probable, the probability that OP makes an angle between $\theta$ and $\theta+d\theta$ with OE is $d\theta/\pi$. We have, therefore, $p(r)dr=d\theta/\pi$, and from (7)

$$d\theta=\frac{9r\,dr}{8\left[1-\left(2\frac{9}{16}-\frac{9}{16}r^2\right)^2\right]^{\frac{1}{2}}}. \qquad \ldots\ldots(8)$$

The result given in section 5 (equation (4)) follows directly.

## § 2. THE 4-LINK CHAIN

*The $\phi$-function.* Referring to figure 5, the link OB rotates about OX at an angle $\alpha$, and BA (or BL) rotates about OB at the same angle $\alpha$. It is required to find the probability that the line OA should make a given angle $\phi$ with OX.

Consider first that OB is fixed in the plane XOY. Let CK be drawn perpendicular to OY, and AP perpendicular to LM, LM being the diameter in the plane XOY of the circle (centre C) described by the rotation of BA about OB. It follows that AP is parallel to OZ. Hence, if PD is drawn perpendicular to OX, AD will also be perpendicular to OX.

If $\phi$ is the angle AOD, we have, therefore,

$$\cos\phi=\mathrm{OD}/\mathrm{OA}=(\mathrm{CK}+\mathrm{CP}\sin\alpha)/\mathrm{OL}=(\mathrm{CK}+\mathrm{CA}\sin\alpha\cos\theta)/\mathrm{OL},$$

where CA makes an angle $\theta$ with CM. This relation between $\theta$ and $\phi$ may be written in the form

$$\theta=\arccos\left(\frac{\mathrm{OL}\cos\phi-\mathrm{CK}}{\mathrm{CA}\sin\alpha}\right)=\arccos(1{\cdot}837\cos\phi-\tfrac{1}{2}).$$

By a similar argument to that in the preceding section the probability of $\phi$ lying below a certain value is then

$$\int_{\phi_0}^{\phi}p(\phi)d\phi=\frac{1}{\pi}\arccos(1{\cdot}837\cos\phi-\tfrac{1}{2}), \qquad \ldots\ldots(9)$$

where $\phi_0$ is its value for the position OM.

For a given value of $\theta$, the rotation of the system OBA about OX as axis will not alter the value of $\phi$. Equation (9) therefore gives the probability that $\phi$ lies between given limits in the case of the 2-link system in rotation. It is, therefore, a solution to the problem stated above.

*The r-distribution function.* Considering now the 4-link chain, let AB and BC (figure 6) be fixed, and let the last two links be replaced by the line CE of length 1·633 (OL in figure 5), making an angle $\phi$ with BC. If P is the instantaneous position of E, and $\theta$ the angle EOP, and if AD is perpendicular to OE (and therefore to DP), we have the following relation between $r(=\mathrm{AP})$ and $\theta$:

$$r^2=\mathrm{AD}^2+(\mathrm{DO}^2+\mathrm{OP}^2-2\mathrm{DO}\,.\,\mathrm{OP}\cos\theta).$$

Insertion of the numerical values gives

$$r^2=5{\cdot}34+4{\cdot}36\cos\phi-3{\cdot}08\sin\phi\cos\theta,$$

leading to the integral distribution of the $r$-values, *for a given value of $\phi$*,

$$\int_{r_0}^{r}p(r)dr=\frac{1}{\pi}\arccos\left(\frac{5{\cdot}34+4{\cdot}36\cos\phi-r^2}{3{\cdot}08\sin\phi}\right), \qquad \ldots\ldots(10)$$

where the lower limit $r_0$ is itself a function of $\phi$.

*The variation of $P(r)$ when $r$ approaches $r_m$.* By an argument analogous to that used later in connection with the "tail" of the multi-link chain, the details of which will not be considered, it may be shown that for small values of $r_m - r$ (where $r_m$ is the upper limit of $r$) $P(r)$ is proportional to $(r_m - r)^{-\frac{1}{2}}$, and hence tends to infinity as $r_m$ is approached. This inverse quarter-power relationship is found to fit the curve of figure 4 reasonably accurately from $r = 3{\cdot}12$ to $r = 3{\cdot}25$ ($r_m = 3{\cdot}27$).

## § 3. THE 5-LINK CHAIN

To define $r$ in terms of $\phi$ and $\psi$ we consider AB (figure 7) fixed while CE rotates. The construction is the same as in figure 6, and we have

$$r^2 = \mathrm{OP}^2 = \mathrm{AD}^2 + (\mathrm{DO}^2 + \mathrm{OP}^2 - 2\mathrm{DO}\,.\,\mathrm{OP}\cos\theta).$$

Also
$$\mathrm{AD} = 1 + 1{\cdot}633\,(\cos\phi + \cos\psi),$$
$$\mathrm{DO} = 1{\cdot}633\sin\psi,$$
and
$$\mathrm{OP} = 1{\cdot}633\sin\phi.$$

Thus, on simplification, it is found that

$$r^2 = 6{\cdot}34 + 3{\cdot}27\,(\cos\phi + \cos\psi) + 5{\cdot}34\cos\phi\cos\psi - 5{\cdot}34\sin\phi\sin\psi\cos\theta.$$

This leads to the following integral distribution of $r$-values, for *given* values of $\phi$ and $\psi$ :

$$\int_{r_0}^{r} p(r)dr = \frac{1}{\pi}\arccos\left(\frac{6{\cdot}34 + 3{\cdot}27\,(\cos\phi + \cos\psi) + 5{\cdot}34\cos\phi\cos\psi - r^2}{5{\cdot}34\sin\phi\sin\psi}\right), \qquad \ldots\ldots(11)$$

in which the lower limit $r_0$ is a function of $\phi$ and $\psi$.

## § 4. MULTI-LINK CHAINS

*Two links joined at random.* Let AB, BP (figure 8) be two links of respective lengths $r_1$ and $r_2$, joined at random. It is required to find the probability $p(r)$ of a given distance $r$ between the ends of the 2-link chain.

Let BP be the shorter link. Then P may be any point on a sphere of centre B and radius $r_2$. If $dx$ is the thickness of a zonal strip of this sphere, perpendicular to AB, and distant $x$ from B, the probability that P lies in this strip is proportional to its area, and is given by

$$\frac{2\pi r_2\,dx}{4\pi {r_2}^2} = \frac{dx}{2r_2}. \qquad \ldots\ldots(12)$$

All points on the zonal strip give the same value of $r$, viz.,

$$r^2 = \mathrm{AP}^2 = {r_1}^2 + {r_2}^2 + 2r_1 x,$$

whence
$$dx = r\,dr/r_1.$$

The probability that $r$ lies between $r$ and $r + dr$ is, therefore, from (12),

$$p(r)dr = \frac{1}{2r_2}\cdot\frac{r}{r_1}dr = \frac{r\,dr}{2r_1r_2}*, \qquad \ldots\ldots(13)$$

where $r$ lies between the limits $r_1 - r_2$ and $r_1 + r_2$.

* This formula occurs in Rayleigh's paper (1919).

*Method of plotting and calculation of* $P(r)$. Equation (13) may be transformed to

$$\left[\frac{1}{r}p(r)\right]_{r_1-r_2}^{r_1+r_2} = \frac{1}{r_1 r_2}.$$

A plot of $p(r)/r$ against $r$ is, therefore, represented by a horizontal straight line extending from $r = r_1 - r_2$ to $r = r_1 + r_2$. This renders the numerical operations simpler than might have been expected. The summation of the elementary distributions can be reduced to the addition and subtraction of numbers, since $p(r)/r$, for given values of $r_1$ and $r_2$, is simply a constant. The summation process gives $P(r)/r$ for the chain, which when plotted is represented by a saw-edged curve. The discontinuities are due to the use of finite elements instead of infinitesimals in the combination of the two distribution functions $p(r)$. The peaks were smoothed out by drawing a suitable continuous curve, and from it the values of $P(r)$ were directly obtained.

*Special method of obtaining* $P(r)$ *when* $r$ *is large.* In compounding two $Z$-link curves to produce the $2Z$-link distribution, the long exponential type of "tail" of the $Z$-link curve (i.e. when $Z$ is large) permits of the adoption of a contracted method, in the region of large $r$ values, which saves a good deal of labour.

In dividing the original $p(r)$ function into elements, and carrying out the process described in section 9, it is apparent that, owing to the limits imposed on the function (13), the value of $P(R)$ for the $2Z$-link chain at a particular value of $R$ is dependent only on those elements for which $r$ is equal to or greater than $\frac{1}{2}R$. Now, for a rapidly diminishing exponential curve, the probabilities associated with successive elements are of different orders of magnitude; elements corresponding to $r > \frac{1}{2}R$ may therefore be neglected in comparison with the element corresponding to $r = \frac{1}{2}R$. The value of $P(R)$ in this region is, therefore, effectively determined by the single element at $r = \frac{1}{2}R$, those on the one side not being involved, and those on the other side being negligible. By representing the "tail" successively on different scales (e.g. differing by a factor of 10) the values of $P(R)$ over the whole range of $R$ are thus readily obtained. A detailed examination of the approximations involved in this contracted method shows that it tends to give $P(R)$-values which are too high. The errors involved are, however, not serious in relation to the very rapid variation of $P(R)$ with $R$.

The method was tested by applying it to the case of the combination of two distribution functions corresponding to the Kuhn formula. This formula should apply accurately if $Z$ is large, provided that $r$ is small compared with its maximum value $r_m$. The combination of two $Z$-link Kuhn distributions must, therefore, produce the Kuhn $2Z$-link distribution, subject to this limitation on $r$. Application of the preceding method to the 750-link Kuhn chain yielded the following figures for $P(R)$ for the 1500-link chain. These are compared with the Kuhn values for the 1500-link chain.

| $r$ (750-link) | $R$ (1500-link) | $P(R)$ Contracted method | $P(R)$ Kuhn (1500) |
|---|---|---|---|
| 100 | 200 | $1{\cdot}6 \cdot 10^{-9}$ | $1{\cdot}05 \cdot 10^{-9}$ |
| 110 | 220 | $2{\cdot}0 \cdot 10^{-11}$ | $1{\cdot}7 \cdot 10^{-11}$ |

The values of $P(R)$ calculated by the contracted method are, as was expected, rather too high.

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# RAY TRACING THROUGH NON-SPHERICAL SURFACES

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RAY tracing through non-spherical surfaces differs from the normal method applicable to those which are of spherical shape, although the fundamental principles are the same. Each ray has to be defined by means of two parameters connected with it, usually the inclination to the axis and the position at which the axis is crossed or would be crossed if the ray were continued far enough. The point of intersection of the ray with the next refracting surface is determined and the inclination found of the normal to the surface at the point. The refraction equation can be applied, and the inclination of the refracted ray then becomes available as well as the point at which the new ray cuts the axis. Then the process is repeated for the next surface. The difference between spherical and non-spherical surfaces lies in the manner in which the point of intersection of the ray and the surface is found. For the sphere the simple formulae of trigonometry can be used; for non-spherical surfaces these are not suitable, and some algebraic solution has to be carried out which will be more and more tedious as the degree of the equation of the generating curve is raised. For this reason I strongly advocate that any attempt to design non-spherical systems should be restricted to spheroids—that is to say, to the surfaces obtained by rotating conics round their principal axes. Nothing higher than quadratic equations will then be encountered.

The primary reason for the desire to utilize non-spherical surfaces lies in the fact that each surface yields at least one extra parameter that can be used for the elimination of aberrations *without alteration of the paraxial conditions.* If the generating curve is a conic, making the surface a spheroid, one parameter only is available; if the curve is of higher degree, more than one. If axes of co-ordinates be chosen so that $Ox$ lies along the optical axis and $Oy$ is at right angles to it, the equation of the generating curve must be of the form $y^2 = 2rx - px^2 + qx^3$, etc., where $r$ is the radius of curvature of the surface at the vertex. The quantities $p$, $q$, etc., are arbitrary and can be used by the designer to get rid of the aberrations that will arise from large apertures and fields. The

first alone of these enters into the aberrations of the first order, $p$ and $q$ into the second order, and so on. In restricting the surfaces to spheroids, the equation of the generating curve must stop short at the second term on the right-hand side. This does not mean that higher-order aberrations than the first cannot be dealt with, but that the $p$'s for the various surfaces must be so chosen that the final image is as free from defect as it is possible to make it. With spherical surfaces the only thing that can be changed in the curve is its radius. This affects the position and size of the paraxial image, so that at least one other surface has to be altered to restore matters. This point is exemplified by a single thin lens. Its power can be kept constant if the difference of the curvatures of its surfaces remain the same. The mean curvature is consequently at the designer's disposal. He has, in fact, one parameter available for the purpose of varying aberration. With non-spherical surfaces there is one extra variable available for each surface. It is obvious that the designer is in a much more

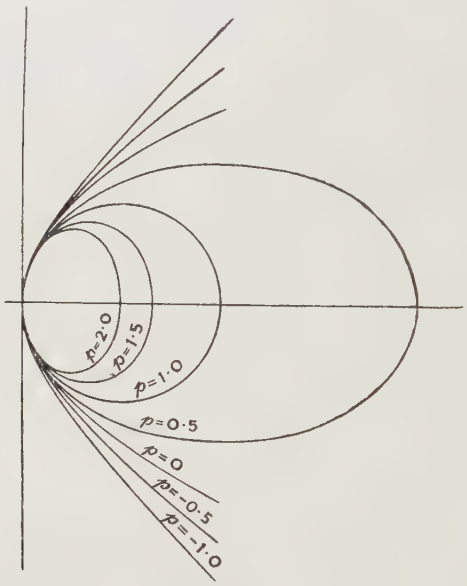


**Figure 1.**

favourable position. It is undoubtedly this scarcity of variables that has led to the large number of elements that have to be used in photographic lenses of wide aperture and field.

Before going on to the formulae for ray tracing it is advisable to consider the kind of curve that the equation $y^2 = 2rx - px^2$ can represent. Its form shows that it is a conic with one principal axis along O$x$ and the other parallel to O$y$. The curve cuts O$x$ at $x = 0$ and at $x = 2r/p$. The length of one semi-axis is thus $r/p$ and that of the other is the value of $y$ when $x = r/p$—that is to say, it is $r/\sqrt{p}$. Both these quantities are real if $p$ is positive. The curve is then an ellipse. The long axis lies along O$x$ if $p$ is less than one; the short one along O$x$ if $p$ is greater than one. Intermediately, if $p = 1$, the curve is a circle. When $p = 0$ the curve is a parabola with its axis along O$x$. For negative values of $p$ the curves are all hyperbolas with the real axes along O$x$. The curves are shown in figure 1 for $p = 1{\cdot}5,\ 1{\cdot}0,\ 0{\cdot}5,\ 0,\ -0{\cdot}5$. All curves of the family have four-point contact with one another at the origin, and consequently, being curves of the second

degree, cannot cut one another at any other point. The ellipses lie successively inside one another as $p$ increases, and ultimately we arrive at a curve of no aperture at all, but still having the standard radius of curvature, $r$, on the axis. It thus appears, from a practical point of view, that there will seldom be occasion to make use of values of $p$ exceeding 3 or 4 on the positive side—that is to say, where the curve deepens at the edge. On the negative side slightly larger values may be encountered, possibly going up to 6, but for any larger values there is such a difference between the two principal radii of curvature that it is hardly likely that astigmatism will have become so bad as to need such drastic correction.

In figure 2 let a ray strike the surface at a point P and be directed towards the point O on the axis distant $u$ from the vertex, V, of the curve. The refractive indices of the two media are $n$ and $n'$, and the refracted ray cuts the axis in I. The slope of the initial ray is $t$ and the equation of the ray is seen to be $y = t(u - x)$. The equation of the curve is $y^2 = 2rx - px^2$. The $x$ co-ordinate of the point P is given by the equation

$$(p + t^2)x^2 - 2x(ut^2 + r) + u^2t^2 = 0.$$

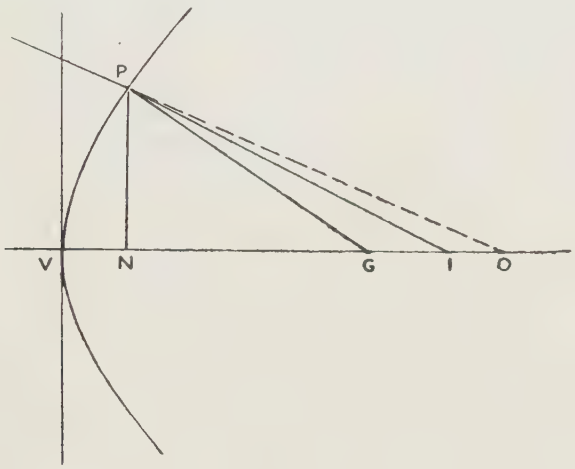


Figure 2.

It is the smaller root of this equation, namely $\dfrac{r + ut^2 - \sqrt{(r + ut^2)^2 - u^2t^2(p + t^2)}}{p + t^2}$, that is required. Having obtained the $x$, the $y$ of the point P can be calculated from either equation.

The inclination of the normal PG has then to be calculated, and also its length, since it is the secondary radius of curvature, and will be needed in the determination of the astigmatism curves. The length of the sub-normal NG is $y\,dy/dx$ or $r - px$, where the $x$ is the abscissa of the point P. PG can thus be easily found.

The primary radius of curvature is found by the ordinary Cartesian formula $\dfrac{\{y + (dy/dx)^2\}^{3/2}}{d^2y/dx^2}$ and will be found to reduce to $PG^3/r^2$, which is convenient for the purpose of logarithmic computation.

The solution of the quadratic equation is straightforward but laborious. The work could be shortened by the compilation of a special set of tables. If

we write it in the form $ax^2-2bx+c=0$, the smaller root is $x=(b-\sqrt{b^2-ac})/a$, which is equal to $(b/a)(1-\sqrt{1-X})$, where $X$ stands for $(c/b)/(b/a)$. In the process of computation by logarithms we shall arive at the value of $\log X$, and then make use of a table in which $\log(1-\sqrt{1-X})$ is expressed for a whole range of values, using $\log X$ as argument. This table would be in two parts, one for positive and the other for negative values of $X$. For the positive values the upper limit of $X$ is unity and the lower about 0·05. The negative values of $X$ would start at the same lower limit, but it is difficult to be sure, until one has actually tried the tables, how far it might be necesary to extend them upwards in order to cope with all ordinary optical computation. When the value of $X$ is small, that of $x$ will be small also. In this case the quickest method of arriving at the solution is by successive approximation. Write the equation as $x=\frac{1}{2}c/b+\frac{1}{2}ax^2/b$. The first approximation to the solution is $\frac{1}{2}c/b$. By putting this in on the right-hand side we get a closer approximation, $x=\frac{1}{2}c/b+ac^2/8b^3$. The new value of $x$ is now used in computing the value of the correcting term $\frac{1}{2}ax^2/b$, and the process repeated until no further change is made in it. Provided the value of $x$ is small enough (and it is only in such cases that this method of solution is justified), the true value is found in two approximations at most, and the computation of $\frac{1}{2}ax^2/b$ can be done by slide rule.

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# THE CHEMICAL AND PHYSICAL PROPERTIES OF LUMINESCENT MATERIALS

By J. W. STRANGE

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## § 1. INTRODUCTION

In the last few years luminescence has risen from being a curiosity of slight academic importance to being the basis of new and important industries. There has been a tremendous increase in the number of patents and papers referring to it; a number of scientific bodies have held conferences or meetings with luminescence as the principal subject, and it is very appropriate that the Colour Group of the Physical Society should also devote one of its meetings to its consideration. It is certain that in the future the colour questions raised by one section of the subject alone, fluorescent discharge lamps, will be many and varied.

In introducing this subject, it may be interesting to trace briefly its development. Such a treatment may explain in part the distinctly alchemical, if not culinary, flavour which still pervades the preparation of phosphors. The long phosphorescent decay of such materials as zincblende and fluorite have probably been known for centuries. Among the first phosphors to be artificially prepared were the Bolognian phosphorus made in about 1700 by heating barium sulphate and flour together, and Canton's phosphorus made by heating oyster shells and sulphur. Success in these preparations must have depended to a large extent on being lucky in the choice of starting material, because it was not until the latter half of the nineteenth century that the importance of traces of heavy metals

such as Cu and Bi as *activators* was realized. Balmain's CaS . Bi, first used in 1877, is a well known case of an early application of this discovery. Another feature in the general method of preparation of phosphors, which was very much in dispute then, and, in fact, still is to a certain extent, was the function of various salts added as *fluxes*. Apart from the usual properties of aiding combination and fusion, it was claimed by some that they formed an essential part of the phosphor. C. Henry stated that chlorides were essential in the preparation of ZnS, and modern opinion confirms this, but Lenard and his school went further, and the accepted recipe—a word with very appropriate connotations—for CaS . Bi stipulates the addition of 0·024 % Bi, 5 % $Na_2SO_4$, 2·5 % $Na_2B_4O_7$, and 2·5 % $CaF_2$. One of the probable effects of such additions was to maintain a non-oxidizing atmosphere during the heating or activation process, but almost certainly the final result of such a process would be an ill-defined mixture partly composed of CaS, $CaSO_4$, CaO and the fluxes—a hopeless starting point for any investigation of physical properties.

This lack of rigid chemical control and of co-operation between chemist and physicist has accounted for a good deal of the lack of progress in understanding luminescent phenomena. A great deal of the published matter on luminescence is of little or no value. Only recently a paper was published giving the results of some measurements made on a phosphor "of unknown origin", a fact which greatly reduced its value.

In addition to this disadvantage there has been the added hindrance of lack of clarity in the terms used in describing the effects observed. *Luminescence* is the term rightly used to cover the whole range of phenomena, but the other terms, *fluorescence* and *phosphorescence*, have also been used to cover the same ground. Some increase in clarity was obtained by confining fluorescence to light emitted during excitation and phosphorescence to the light emitted after excitation has ceased. This definition is still arbitrary and inexact; a basis for a more accurate definition will be discussed later.

The term *phosphor* has firmly established itself to mean a fluorescent material. Luminophor and fluor may be more exact in certain cases, but, in this paper at least, the more traditional term will be used.

Luminescence is not, of course, confined to inorganic solids of the type mentioned. It is very widespread in its occurrence among gases, liquids and solids. It can be excited by light in the visible or ultra-violet regions, by cathode rays, X rays or $\alpha$ particles. There are also more unusual types, distinguished by a special terminology; luminescence produced by grinding is called triboluminescence, by heat thermoluminescence, by chemical reactions chemiluminescence, by biological reactions bioluminescence.

As a consequence of this widespread occurrence, luminescence has importance in a number of ways in addition to the main ones, with which we shall deal later. For example, its analytical possibilities are considerable, once a reliable source of ultra-violet light is obtained (Radley and Grant, 1935); it is, however, difficult to say how far they have been realized. Reports have been made that the age of eggs can be determined very exactly by the fluorescence of the watery solution of the albumen, and that the maturing of cheese can be followed by the change in its fluorescence from yellow to blue with age; but the extreme sensitiveness of some of such effects to traces of impurities may destroy their reliability for

general use. The claim that the fluorescence excited in various white pigment materials, such as ZnS, CaO, MgO, $TiO_2$, can be used for distinguishing between them is very open to doubt in the light of our present knowledge of the influence of impurities and heat treatment on such materials.

In spectroscopy, luminescence is chiefly notable as a possible source of considerable error in spectrophotometric work, where, as in the latest Hardy instrument, the light is dispersed before falling on the sample.

In atomic physics it has played an important, but subsidiary, part in detecting particles and radiation of different types. The work now being done on the properties of luminescence in gases, liquids and solids should make increasingly important contributions to our knowledge of the structure of matter.

The oldest application of luminescence is in the use of the phosphorescent decay of such materials as CaS.Bi and ZnS.Cu to improve the visibility of objects such as watch-dials at low intensities of illumination. This is now usually supplemented or superseded by the fluorescence excited by radioactive materials incorporated in the layer. There is an interesting topical application of the same idea in the test for night vision devised by W. D. Wright, where a layer of the latter type provides a practically constant source of low-level illumination.

## § 2. LUMINESCENCE IN INORGANIC SOLIDS

In the remainder of this paper our attention will be confined to the restricted field of luminescence in inorganic solids. This limitation is made because it is for materials of that type that the very important industrial applications of to-day have been found. These applications are in two main groups: phosphors in cathode-ray tubes used either as monitors for electrical signals or as essential units in a television system, and phosphors in gas discharge-tubes for lighting. Both of these were suggested many years ago. Luminescent materials as a means of supplementing the light output from a discharge were proposed towards the end of the nineteenth century, but it was not until 1933 that the idea received commercial application in this country; it quickly proved able to give an efficiency of 35 l/w. compared with the 12 l/w. of the tungsten-filament lamp, and, as an indication of its very rapid rise in importance, we may give the following figures for the production of fluorescent discharge-tubes during recent years in the U.S.A. (*American Exporter*, June 1492):—

| | |
|---|---|
| 1939 . . . . . | 1,000,000 |
| 1940 . . . . . | 7,100,000 |
| 1941 . . . . . | 22,000,000 |

Appreciation of the possibilities of the cathode-ray tube followed close on the production of the Braun tube, the earliest form. About 1908, Campbell Swinton and others made the suggestion that it could be used for the transmission and the reception of light images. It was not until after 1930 that any rapid progress was made along those lines, but by 1936 a high-definition system of television was in operation. Cathode-ray tubes with screens of calcium tungstate, chosen for its rapid decay, were used for the "scanning" of cine film, others with screens of such materials as zinc orthosilicate were used for receiving

the signals. The cathode-ray tube was soon ousted from the transmission end by the iconoscope, but there is no doubt of its supremacy for reception. This is not the place to trace its development in detail; one fact will suffice to illustrate not only the enormous advances that have been made in electron optics in the last few years, but also the way in which phosphors have stood up to the enormously increased demands that have been made on them. In 1936 Levy and West remarked that a power loading on a cathode-ray-tube screen of 0·055 watt per $cm^2$ (i.e. taking the whole scanned patch or raster) was "enormously higher than anything contemplated in television". Within three years the loading possible had, in fact, increased to about 1·0 watt per $cm^2$. This increase is still more remarkable if we consider the loading on the spot under the electron beam and not on the scanned patch; this figure may well be of the order of 25 kilowatts per $cm^2$.

The relation between current and light-output is one of the properties which may help to clarify the understanding of the luminescent process, but up to the present most of the existing theories have been more related to the chemical data than to physical measurements of this type, owing to the lack of the latter.

The theory of active centres was based upon the observed fact that a small addition of some heavy material was needed to produce luminescence in some of the principal materials used. The importance of such impurities was still further appreciated when it was discovered that some metals such as Ni may have a notable effect on the luminescent properties when present in as low a proportion as $10^{-6}$. Extreme purity was, therefore, the first and major consideration in the preparation of the phosphors. The base materials of the phosphors are usually produced from purified chemical stock by precipitation in the cases of sulphides, and by mixing the component oxides in the case of silicates, borates, tungstates, aluminates, etc. The activator is added in some convenient soluble form either during or after this stage. The elements used are very limited in number. Manganese is the most important; it is added in proportions varying from 0·25 to 5·0%, there being an optimum concentration for each material. Chromium and samarium are similar to manganese in the amounts required. The other main group of activators, of which Cu, Ag, Bi, Au and Pb are the best known, have their optimum concentration in the range 0·01 to 0·1%.

After the addition of the activator, the material is fired to temperatures ranging from 850° c. to 1250° c., depending on the material. The object of this firing is to cause the activator to go into solid solution in the base material, to cause combination in the case of the mixed oxides, and to produce a suitable crystalline form. There are empirical rules for each material giving the optimum temperature. For the silicates this is about 1200° c. For ZnS . Ag and ZnS . Cu it is about 950° c., and the firing results in a crystalline form which is partly hexagonal and partly cubic. For ZnS . Mn, on the other hand, the optimum is 1100° c. (It should be added that in the case of all the sulphides the firing has to be done in an inert atmosphere to prevent oxidation.)

Mention has already been made of the part claimed for fluxes in the past. To-day their importance is believed to be negligible with the exception of the preparation of sulphide phosphors. They may in certain cases, such as zinc

orthosilicates, offer the practical advantage that they lower the firing temperature from 1250° C. to 1000° C., but they play no essential part, and the phosphors prepared with them are usually inferior to those prepared without fluxes. In the case of ZnS, on the other hand, the presence of a chloride has a marked effect, the intensity of luminescence being greatly enhanced. The chloride, in this case, appears to be an essential part of the active centre. The following experiment gives support for this suggestion, and at the same time illustrates the extreme sensitivity of these materials. Three silica tubes were taken; in the first some pure ZnS was placed with 0·001% CuS and an equivalent amount of $NH_4Cl$; in the second the $NH_4Cl$ was omitted; in the third the CuS and the $NH_4Cl$ were omitted. The tubes were evacuated and sealed off, and then heated to 1000° C. for several hours. On testing, the first showed the luminescence characteristic of ZnS . Cu, but the other two had little or no emission. Similar results were obtained with silver as an activator, but with manganese good results were obtained without a flux. One point that may be significant in this connection is that the lattice dimensions of ZnS and CuCl are practically the same, viz., 5·42 A. and 5·41 A.

Another point which shows the extreme sensitivity of these materials is the peculiarly selective effect which small traces of nickel and, to a lesser degree cobalt, has on the decay of luminescence. Nickel when present in a proportion of one part in two million reduces the intensity and life of the long phosphorescent decay of zinc sulphide, while hardly affecting the intensity of the fluorescence. This effect is made even more interesting by the fact that the same amount of nickel has the effect of producing a long phosphorescent decay in zinc borate.

There is one group of phosphors which we have so far not touched upon, those without added activator. This is a rather controversial issue, for a number of workers, such as Tomaschek, have stated that pure materials such as ZnS do not fluoresce. It is, however, an experimental fact that as materials such as ZnS, the tungstates and zinc silicate are purified—and subsequently given the standard heat treatment—so does their luminescence increase also. It has, however, been recently suggested by Seitz (1939) and others that by a similar process to that advanced for the development of photo-conductive properties in ZnO, the luminescence is due to the production by the heat treatment of a stoichimetric excess of Zn in the crystal lattice. If this view is correct, the luminescence of pure ZnS, ZnO, $Zn_2SiO_4$ and similar phosphors must be classed with ZnS . Ag and other impurity phosphors. Their other properties, such as decay times and emission spectra, are certainly very similar. The case of the tungstates is not so clear, because in the emission spectra of all of them there appears a common band which can be attributed to the $WO_4$ ion. The similarity between luminescent and photo-conductive properties which has led to this suggestion may be over-emphasized, for experience with ZnSe (Miller and Strange, 1938) shows that the two effects are far from being equally sensitive to alterations in conditions of preparation, such as amounts of impurities, although in this case too a stoichimetric excess of Zn was probably responsible for the photo-conductive action.

There is one other matter regarding the chemical constitution of phosphors

which is of particular interest at a meeting of the Colour Group. Guntz discovered in 1926 that the colour of ZnS . Cu could be altered towards the red by the substitution of CdS for part of the ZnS; this also applies to ZnS . Ag, but not to ZnS . Mn. Subsequent investigation showed that there was an exact linear relationship between the peak of the emission band plotted on a frequency scale and the percentage by weight of CdS; but so far no physical theory has been advanced to explain this (Henderson, 1939). It was materials of this type which were soon universally used for cathode-ray tubes, as the accurate colour control made the required white colour easy to obtain by mixture, and their efficiency was high. This was followed by the application of the same idea to zinc silicate for use in cathode-ray tubes and in fluorescent discharge-tubes. This time it was the substitution of BeO for part of the ZnO which caused the colour shift from green to red; there was, in addition, the unusual feature that the amount of manganese used as activator also had the same effect when beryllium was present; when it was absent, change in activator content over a wide range had no effect.

## § 3. MECHANISM OF LUMINESCENCE

The physical explanations of the luminescent process are usually based on the assumption that while any of the atoms of the phosphor may absorb the incident energy, it is the atoms of the activator, or the "active centre", which are responsible for the emission. The simplest case is, however, one in which the addition of the activator produces new absorption bands; if a quantum of light within such frequency limits falls upon the phosphor it is absorbed by the activator atom itself. An electron attached to this atom may then be raised from its ground state to some higher energy state or excitation level, or it may receive sufficient energy to reach the conduction band of the solid and be carried away from the parent atom, leaving a "positive hole", i.e. a process of ionization. The same two possibilities hold for energy absorbed by the atoms of the base material, but with the difference that if it is to result in visible radiation the energy must be transferred to the active centre. This is particularly so in the case of luminescence excited by $\alpha$-particle or cathode-ray bombardment, for in these cases there is no differential absorption by the activator atom and yet the efficiency of these processes is far higher (6 to 10 % for electrons and about 80 % for $\alpha$ particles) than can be accounted for by the small proportion of the total energy which is absorbed by the activator atoms. It is not sufficient to suggest that the ionized electron travels through the conduction band until it reaches the activator atom, because unless the latter is also ionized there will be no positive hole for the electron to fall to and no radiation will be possible. The mechanism suggested by Frenkel (1936) to meet this difficulty is a transfer of energy through the crystal by means of an "exciton" or excitation wave. This is based upon the electrical coupling or resonance between atoms close together in crystals, and involves no accompanying motion of charge. One interesting feature of this suggestion is that it limits the transfer to energies less than those required for ionization, thereby explaining the lower proportion of phosphorescence usually observed in electronic excitation.

The actual emission of light accompanies the return of the electron to its ground state. The rate at which this takes place after absorption of the incident energy gives essential information regarding the process involved. The rate at which the ionized electrons return depends on $n$, the number of electrons, and $n$, the number of positive holes, i.e. it will be proportional to $n^2$ and will be similar to a bimolecular reaction; it will also depend upon the number of lattice defects and other traps which may hold the electron and also the availability of the additional energy necessary to remove them from such traps, i.e. it will be temperature-dependent.

The return of electrons from excitation levels to their ground states is simpler, for it will depend only on inner (atomic, molecular, or also lattice-dependent) transition probabilities. The decay of the fluorescence after excitation has ceased will be similar to a monomolecular reaction and will be exponential in form.

The equations of the two forms are the following:—

$$(a)\ I = I_0/(1-\alpha t)^2;$$
$$(b)\ I = I_0 e^{-\alpha t}.$$

There are, of course, other possible forms involving multiple states, or combining the two described. It may be stated in passing that in this distinction between the two processes (*a*) and (*b*) we have the only applicable distinction between phosphorescence and fluorescence (Perrin, 1929; Pringsheim, 1939).

Taking some examples from electron-excited luminescence, we may say that in certain cases the measured properties of the phosphors fit these simple assumptions. A number of materials, such as ZnS . Cu, have long phosphorescent decays which are bimolecular in form and which are temperature-dependent; $Zn_2SiO_4$ . Mn and other manganese-activated phosphors have exponential decay-forms which are unaffected by temperature. Such agreement is more limited than it appears to be, for in ZnS . Cu, in addition to the slow phosphorescent decay with a half-life of the order of seconds, there are two other forms which change in proportion with intensity of excitation; the slower, which is predominant at low intensities, has a half-life of about 50 microseconds and is apparently exponential in form, while the decay of the other is less than a microsecond. Such complex behaviour is common to all materials activated with Cu, Ag, Bi, Sm, Mo and Pb, and to the group of "pure" phosphors. The half-life of the main exponential process varies from less than a microsecond for ZnO and ZnSe to over 100 microseconds for CaO . Sm.

The materials activated by Mn and Cr fall into a quite separate class with, at low current densities, simple exponential decays having a half-life ranging from about 10 milliseconds for magnesium orthosilicate to 1 millisecond for ZnS . Mn. Recent work has, however, shown that they also change with increase in intensity of excitation and develop a rapid initial drop.

Some attempt has already been made (Gurney and Mott, 1940) to bring theory into line with these experimental results, but much remains to be done on both the theoretical and practical sides before an adequate understanding of the luminescent process is obtained.

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# "KODAK" FLUORESCENCE PROCESS OF AUTOMATIC COLOUR CORRECTION

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*ABSTRACT.* In most photo-mechanical reproduction processes it is necessary to introduce corrections to compensate for deficiencies inherent in the printing inks. Such corrections are usually applied by hand on the printing plates on the intermediate positives or negatives, or by means of photographic *masking*.

The "Kodak" Fluorescence Process provides a simple method of automatically obtaining the required colour correction during the actual process of making separation negatives and eliminates the need for any form of hand re-touching or fine-etching. This is effected by the inclusion in special water-colour paints of materials which fluoresce brightly under ultra-violet radiation, but which do not alter the appearance of the paints under ordinary lighting conditions. In adjusting the amounts of the fluorescent materials included in each paint, the printing inks to be used subsequently were taken into account so that when colour-separation negatives are made using a suitable mixture of ultra-violet and visible radiation, extra density is added to those parts of the negatives requiring attention. The complete set of special paints consists of eighteen water colours, which are applied to a white drawing surface by the artist. The copy is then illuminated by arc lamps covered by a filter unit transmitting ultra-violet mixed with a proportion of blue-violet and green light. An adjustable slit holding compensating filters allows the operator to adjust the balance of illumination so as to ensure proper colour correction. Both yellow and magenta printing negatives are made with the filter unit in position, while the blue-green and black printing negatives are made with unscreened white light illuminating the copy, the latter negative being made on an infra-red sensitive plate.

At some stage in the process of preparing the metal printing plates used in photo-mechanical colour reproduction, it is necessary to make corrections by hand to compensate for inevitable departure from the theoretically correct hue of the printing inks. For relief-printing methods the corrections are made on the printing plates by locally reducing the size of certain of the dots into which the image is broken up in the half-tone process, the operation being known as *fine etching*; in photo-lithography, or photogravure the corrections are by means of hand retouching on the screen or continuous

tone positives. These operations are of a highly skilled nature, requiring considerable knowledge of colour-correction technique as well as manual dexterity on the part of the operator. Some assistance has been provided to the operator by the use of prepared colour charts (Cartwright, 1928; Hallam and Cox, 1932 and 1936; Cackett, 1940), showing the dot sizes needed on the printing plates or intermediate transparencies to produce a desired hue, assuming given printing inks to be used. While it is doubtful whether fine etchers or retouchers rely on their use for long—as they soon become familiar with the various dot sizes required for reproducing the different colours—such charts are of considerable assistance during training, and afterwards for reference purposes.

That this handwork is difficult and uncertain is well realized, and many attempts have been made to introduce colour corrections mechanically, and the so-called *photographic masking* processes have been suggested by many workers for this purpose, probably the earliest suggestion being made by Dr. E. Albert in 1898. In 1934, Alexander Murray, of the Eastman Kodak Company, made a thorough investigation of masking techniques and described the preparation of correcting masks for the yellow and magenta printing negatives of a colour separation set which, if properly carried out and used with selected inks, results in excellent colour reproduction. The method involves the making of two contact positive masks of low contrast from the blue-green printing negative, and binding these into exact register with the yellow and magenta printing negatives, so that wherever blue-green is printed, the corresponding areas of the yellow and magenta negatives are increased in density. This results in considerably improved rendering of blues and greens by automatic removal of unwanted yellow and magenta in place of the manual removal, which is the normal practice. Other masking techniques have been suggested by many workers, generally of a more involved nature than the Murray method, with the aim of extending the range of colours corrected, but all depending on the same principle of utilizing photographic masks in conjunction with the separation negatives or positives. The success of these methods depends on the accuracy with which the operator produces correct characteristic curve shapes and densities in the negatives and masks. If these are not obtained, the reproduction is often unsatisfactory, and sometimes worse than if no correction of this type were attempted. It is probably for this reason that photographic masking does not appear to have made much headway in this country, although the process is said to have had some considerable success in America.

For a colour-correction process to become really useful in process houses as distinct from experimental laboratories it is desirable that the correction be effected automatically during the photographic operations, while yet requiring substantially normal procedure on the part of the operator in preparing the colour-separation negatives. To this end the "Kodak Fluorescence Process" has been evolved by our Rochester Laboratories, and although it must be stated at once that the process is limited to the reproduction of artist-drawn originals prepared with special paints, this covers quite a large proportion of modern colour-work.

The principle upon which the Fluorescence Process depends is the inclusion in the special paints of materials which fluoresce brightly under ultra-violet

radiation, though they appear to be normal pigments under normal lighting conditions, so that when colour separations are made using a suitable mixture of ultra-violet, and visible radiation, the appropriate extra density is automatically added to those negatives which require colour correction. The amount of the fluorescent materials included in each paint is related to the printing inks which will be used for subsequent printing from the plates in such a manner that the colour correction is applied automatically. The special paints comprise a set of eighteen water colours which are as easy for the artist to work with as conventional water colours. The complete set provides a sufficiently wide selection for all requirements, and the range has been deliberately limited to include only those colours which can be reproduced with the best four colour-printing inks available. Because of this, some of the more brilliant pigments included have been intentionally greyed to match the colours which will be obtained on the printing press. Apart, therefore, from the automatic colour-correction, the palette available has the advantage that whatever colour scheme is produced with it, it can be reproduced exactly by four-colour photo-mechanical reproduction.

The artist paints his picture with these colours under normal lighting conditions in which the fluorescence is invisible, and either brush or airbrush techniques may be used. The colours may be mixed with the white supplied with the set to produce opaque effects, or diluted with water to make transparent washes. The artist will have to make a slight modification to his normal technique of producing different hues by mixing colours, since it is important that only colours adjacent to each other on the list of colours supplied be mixed to obtain an intermediate hue, as otherwise the correct fluorescence balance would be upset. To produce greys, combinations of black, browns and white are used, and the artist must not mix complementary colours, as this also would produce the wrong balance of fluorescence.

The art papers or drawing boards used by the artist should be white and as free as possible from inherent fluorescence, and it should be noted that while the colours are sufficiently fast to light for making drawings which are to be reproduced within a reasonable length of time, they cannot be recommended for display purposes, for which use they are not intended.

The colour-separation negatives are made in the camera, using arc illumination, the arcs being placed alongside the camera. For making the yellow and magenta printing negatives, the arcs are shielded by special hoods fitted with filter units which allow ultra-violet, blue-violet and green light to reach the copy. These filter units consist of two panels of glass which transmit ultra-violet only, separated by a channel covered by an adjustable slit into which yellow or magenta compensating filters may be fitted, while the design of the hood prevents any stray light from reaching the copy. It is necessary to adjust the filter units in order to obtain the correct ratio of ultra-violet to visible blue-violet and green light from each of the arc lamps, and this is made possible by varying the width of the central slit, and by inserting magenta or yellow compensating filters in the inner channels behind the narrow blue filters contained in the outer channel. The correct balance is determined by reference to control patches which are placed on the copyboard. These consist of both fluorescent and white paper sheets which are examined through colour filters, and adjustments are

made to the slit width until they match in brightness. It may be necessary to insert compensating filters in order to effect a match; but once this has been done, no further adjustment is necessary. The yellow and magenta printing negatives are made, preferably on orthochromatic plates, using a special blue filter over the lens for the former negative and a Wratten K.2 filter for the latter. To make the blue-green printer, and the black, the filter unit is lowered in its slide, so that unfiltered white light reaches the copy. The blue-green printer is made on a panchromatic plate, an analysis red filter (Wratten No. 29) being placed over the lens. An infra-red sensitive plate is used for the black printer, a filter transmitting infra-red only being on the lens for this operation. The paints have been made with pigments which reflect infra-red strongly, so that a perfect black printing negative is produced.

When the colour chart is irradiated with ultra-violet alone, the full effects of the fluorescent substances are observed. The following chart tabulates the colours of the paints, the fluorescence obtained, and the negatives which are increased in density due to the fluorescence.

| | Colour of paint | Fluorescence | Printing negative on which increased density is produced (Y = yellow, M = magenta) |
|---|---|---|---|
| 1 | Lemon yellow | Green | M |
| 2 | Warm yellow | Degraded green | M |
| 3 | Orange | ,, ,, | M |
| 4 | (Orange-red) | | |
| 5 | Crimson | Blue-violet | Y |
| 6 | Rose | ,, ,, (very bright) | YY |
| 7 | Red-purple | ,, ,, | Y |
| 8 | Violet | ,, ,, (very bright) | YY |
| 9 | Warm blue | ,, ,, (very bright) | YY |
| 10 | Peacock-blue | Light blue | Y, M |
| 11 | Green-blue | Turquoise | Y, M |
| 12 | Green | Green (very bright) | MM |
| 13 | Yellow-green | Yellow-green (very bright) | MM |
| 14 | Raw sienna | Degraded green | M (slight effect only) |
| 15 | (Burnt sienna) | | |
| 16 | (Burnt umber) | | |
| 17 | (White) | | |
| 18 | (Black) | | |

The paints shown in brackets in the above table produce very little or no fluorescent effect. YY or MM indicates considerable increase in density.

In order to demonstrate the process, a colour chart was prepared, consisting of flat areas of each of the sixteen colours, with one each of black and white.

Three patches were included for each colour as:—

(*a*) full-strength paint;

(*b*) tints, obtained by diluting (*a*) with water;

(*c*) shades, produced by adding the No. 18 black to (*a*).

This chart was photographed on to suitable Kodak plates to give four-colour continuous-tone negatives. The illumination consisted of 15-a. open arc-lamps placed on either side of the copyboard, and screened by the filter unit which was fitted into a suitable box, the lamps being first balanced visually by reference to the colour patches.

From these negatives, a set of carefully matched 133-line screen positives were made in the normal manner, though with no colour retouching.

Photolitho plates were then prepared from the positives, and proofed, the inks used being the best three-colour set readily available and a black. Comparison of this proof with the original showed that the majority of colours were remarkably well reproduced, and it was particularly noted that magentas, blues and greens, which normally require a considerable amount of handwork, matched the original.

A comparison result was obtained by going back to the camera stage, and making further yellow and magenta printing negatives to unscreened white light. In these circumstances, the fluorescent effect was negligible, so that the negatives were without colour correction. Screen positives, etc., were made and the printing plates proofed up with the uncorrected blue-green printing plate and the black. As would be expected, the reproduced colours of this proof differed widely from the original, but formed a useful basis for gauging the amount of handwork necessary.

For completely faithful reproduction of the original by this method, the hues of the four colour-printing inks should correspond to those for which the fluorescent paints have been balanced. Almost any good set of four-colour inks, however, yields results which are near enough to facsimile for most commercial purposes.

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# EXAMINATION OF THE BERTHELOT METHOD OF MEASURING TENSION IN LIQUIDS

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*ABSTRACT.* The Berthelot method of measuring hydrostatic tension in liquids yields values of the order of 150 atmospheres. A modified Berthelot method in which the pressure at the moment of sealing is known has not given values greater than 25 atmospheres. This order of magnitude is in agreement with the values obtained by the viscosity-tonometer method. The conclusion is reached that falsely high values can be obtained by the ordinary Berthelot method due to the high pressure liable to exist in the final bubble before the tube becomes completely filled by the expanding liquid.

## §1. INTRODUCTION

Attention has previously been drawn (Vincent, 1941, 43) to the remarkably high values of hydrostatic tension which can be deduced from experiments on liquids in sealed tubes when first expanded by heat to fill the tube, then cooled until a break occurred, in accordance with the procedure first employed by Berthelot (1850). Berthelot found that water could thus be made to increase its volume by 0·24 %. By assuming that the extensibility of the water under tension was the same as its compressibility, he deduced that the observed extension would correspond to a tension of about 50 atmospheres. Berthelot also made similar experiments with many other liquids and solutions. In one of these experiments he estimated a tension of 100 atmospheres in sugar solution, and a tension of 150 atmospheres in ether.

Using the Berthelot method, Dixon and Joly (1895) carried out some experiments to find out if water adhered to the conducting tubes of plants sufficiently vigorously to transmit the stress needed to raise the transpiration stream. A small piece of wood was inserted in the tube and a tension of 7 atmospheres was estimated for water in the presence of the wood.

In 1909 Dixon described some further experiments by the Berthelot method in which he deliberately left a trace of air before sealing the tube. A small piece of yew wood was enclosed in one of the tubes, and in another some minute copper shavings. High values of tension could be obtained in all cases, but in the tube having no solid insertions values up to 150 atmospheres were obtained. It is important to notice that Dixon's high results were obtained in spite of the trace of air deliberately included when making the final seal.

Using the method of Berthelot, one of the present authors (loc. cit.) has previously published results of 157 atmospheres for water and 119 atmospheres for mineral oil. Other methods of measuring tension in liquids do not give such high results. The viscosity-tonometer method, which is believed to be reliable, was derived as a first step in the investigation of high values of tension

produced by the Berthelot method. Although comparison of the results by these two methods did not yield an explanation of the relatively high results by the Berthelot method, the experiments did throw considerable doubt on the high values which the Berthelot method yields. It has been the object of the experiments described in the present paper to discover the reason, or reasons, for these relatively high results, which were believed to be probably in error, although the causes of error were not established. The question is: Do tensions of the order of 150 atmospheres really exist inside a Berthelot tube?

## § 2. DESCRIPTION OF EXPERIMENTS BY THE BERTHELOT METHOD

### *Preliminary experiments on water*

It was decided that the first experiments on the Berthelot method would be carried out with water, on account of the historical interest of measurements on this liquid. A suitable size of capillary tube was selected, which was approximately 2·5 mm. bore and 2·5 mm. wall thickness. Two 20-cm. lengths of tube were taken, each sealed at one end and drawn down to a small diameter at a distance of 10 cm. from the sealed end. The tubes were then boiled in a mixture of chromic acid and sulphuric acid to clean them thoroughly. They were then boiled for a long period in distilled water to remove the solution. After this, they were transferred to a tall Pyrex tube of distilled water, and were boiled for 3 hours and allowed to cool down before removal.

To avoid the inclusion of air, the final sealing operation was carried out under vacuum. A rotary vacuum pump with a $P_2O_5$ moisture trap was connected by means of a rubber tube to the open end of one of the 20-cm. lengths. It was found that the water level very gradually fell, due to evaporation from the top meniscus. With a view to retaining as much water as possible in the tube, but at the same time lowering the meniscus clear of the sealing point, ice was applied to the lower half of the tube to contract the water therein. When the water surface had fallen to a level just below the constriction, a small gas flame was applied to the constriction and the lower half of the tube drawn off, thus making an air-tight seal all in one operation. The sealing of tubes under vacuum in this way is not at first easy, but can be achieved successfully after a little practice. The first tube was attached to the bulb of a mercury thermometer and suspended in a 1-litre beaker containing a mixture of about equal volumes of glycerine and water. This mixture prevents the formation of bubbles on the interior surface of the beaker and on the outside of the Berthelot tube, and a clear view of the interior of the tube is obtainable throughout the measurements. An electrically-driven laboratory stirrer was set up so as to keep the liquid in the beaker circulating vigorously.

The procedure adopted was to heat the beaker by means of a Bunsen burner, the rate of heating being reduced as the state of complete fullness of the tube was approached. In this way it was possible to note with precision the bath temperature at which the last bubble disappeared, and the tube became completely filled with water. Cooling was carried out very cautiously by reducing the heat applied to the beaker, and the Berthelot tube was carefully watched for

the first appearance of a bubble. This reappearance was usually accompanied by a metallic click. It was essential, however, that close attention should be paid to the reading of the thermometer, so that no time lag occurred between the breaking of the column and the observation of the temperature. This whole procedure was repeated several times for each tube, and the observations made are set out in the table below:—

Table 1. Distilled water: first tube

| Temperature of bath when heating started (° c.) | Sealing temperature (° c.) | Highest temperature reached (° c.) | Temperature at which water column broke (° c.) | Temperature difference (° c.) |
|---|---|---|---|---|
| 20 | 92·0 | 93 for 5 hours | 86·1 | 5·9 |
| 20 | 92·0 | 95 for 5 hours | 85·0 | 7·0 |
| 85 | 92·0 | 112 | 83·7 | 8·3 |
| 20 | 92·0 | 112 | 83·8 | 8·2 |
| 20 | 91·5 | 120 | 82·0 | 9·5 |
| 20 | 92·0 | 112 | 81·5 | 10·5 |
| 20 | 92·5 | 115 | 79·5 | 13·0 |
| 20 | 94·0 | 120 | 80·0 | 14·0 |
| 20 | 94·0 | 120 | 84·0 | 10·0 |
| 84 | 94·0 | 120 | 83·5 | 10·5 |
| 84 | 94·0 | 120 | 84·0 | 10·0 |
| 84 | 94·0 | 120 | 84·0 | 10·0 |
| 60 | 94·0 | 120 | 89·0 | 5·0 |
| 20 | 94·0 | 120 | 91·0 | 3·0 |
| 20 | 94·0 | 120 | 90·0 | 4·0 |
| 22 | 95·0 | 120 | 88·5 | 6·5 |
| 88 | 94·0 | 120 | 91·0 | 3·0 |

Table 2. Distilled water: second tube
Tube boiled in distilled water for 8 hours

| Temperature of bath when heating started (° c.) | Sealing temperature (° c.) | Highest temperature reached (° c.) | Temperature at which water column broke (° c.) | Temperature difference (° c.) |
|---|---|---|---|---|
| 20 | 69·0 | 69 | 62·0 | 7·0 |
| 62 | 69·0 | 100 | 58·0 | 11·0 |
| 20 | 68·0 | 100 | 57·5 | 11·5 |
| 57 | 69·0 | 100 | 56·0 | 13·0 |
| 20 | 69·0 | 120 | 54·0 | 15·0 |

Tube broke at sealed end at between 100° c. and 120° c.

The theory of the method of calculation to be used for the derivation of the tension from the above results is given below.

Let the temperature at which the tube just becomes full be $T$° c. and the internal volume of the tube at this temperature be $V$ c.c. On cooling, let the liquid column break at $t$° c., the volume of the tube at this temperature being $v$ c.c., and the liquid immediately after the " break " being $w$ c.c.

The extension $E$ per unit volume of the liquid at $t°$ C. is given by $E = \frac{v-w}{w}$; now $v = V[1-3a(T-t)]$, where $a$ is the linear coefficient of expansion of glass, and $w = VD/d$, where $D$ is the density of the liquid at $T°$ C. and $d$ the density at $t°$ C.

Therefore extension per unit volume is

$$E = \frac{1-3a(T-t)-D/d}{D/d}.$$

Substituting values corresponding to the best result in table 2, $E = 0{\cdot}00777$. In the above substitution, $a$ for soda glass has been taken as $8{\cdot}5 \times 10^{-6}$. The density of water at the sealing and breaking temperatures was taken from Kaye and Laby's tables. If $e$ is the volume elasticity of the liquid,

$$\text{Tension} = \frac{E}{e} = \frac{0{\cdot}00777}{48{\cdot}9 \times 10^{-6}} \text{bars} = 159 \text{ bars} = 157 \text{ atmospheres.}$$

The value of the volume extensibility $e$ for water has been taken as $48{\cdot}9 \times 10^{-6}$ per bar, i.e., making the assumption usually made in the Berthelot method of taking the extensibility as numerically equal to the compressibility.

*Experiments on mineral oil*

It was decided next to carry out some experiments by the Berthelot method, using one of the liquids which had already been used in the bellows apparatus (Vincent, 1941), and for this purpose the mineral oil was selected. It will be remembered that the mineral oil gave the highest result in the bellows apparatus. This liquid may therefore be regarded as of special interest in this investigation.

Before starting on the actual tension determinations, some preliminary experiments were carried out to see if any appreciable difference in temperature normally arises between the interior of the Berthelot tube and the surrounding liquid. Several experiments were carried out by means of insulated thermocouples connected differentially, one junction being inside and one outside a tube of the same dimensions as the Berthelot tubes. Under normal conditions the temperature difference was always less than 0°·3 c. This possible error is, therefore, not of great magnitude, and can be almost eliminated by adopting slow heating and cooling.

Having completed the above preliminary investigation, the oil was prepared for the Berthelot experiments by filtering it hot through two filter papers into an evacuated flask. Three Berthelot tubes were then prepared as before and placed open end uppermost in a tall Pyrex glass tube about 1 inch internal diameter. The filtered oil was poured in so as to cover the tubes, and arrangements were made to apply vacuum over the surface of the oil. The tubes were heated in the oil to a temperature of about 120° c. for 6 hours, the absolute pressure being maintained at about 0·5 mm. Hg during this period. The oil was then allowed to cool overnight and the tubes removed when required.

The method of sealing employed was very similar to that previously described in the case of water, vacuum being applied to the end of the tube during the process. The only difference was that the oil column was caused to break in the region to be sealed by heating the drawn-down part of the tube with a small

gas flame. When a suitable gap in the column had been produced the tube was heated more strongly, so that it collapsed under the applied vacuum and was drawn out simultaneously, thus making a permanent seal.

The procedure adopted in measuring the sealing and breaking temperatures was as previously described for the experiments on water. The summarized results are given below:—

| | Number of experiments | Maximum temperature difference observed (° c.) | Sealing temperature (° c.) | Highest temperature reached (° c.) | Breaking temperature (° c.) |
|---|---|---|---|---|---|
| First tube | 7 | 6 | 40 | 60 | 34 |
| Second tube | 11 | 12 | 59 | 70 | 47 |
| Third tube | 6 | 11 | 36 | 46·5 | 25 |

In calculating the tension from the above results the usual assumption has been made that the extensibility of the oil is numerically equal to its compressibility. The value of the compressibility has been taken as $62 \times 10^{-6}$ per bar, given in Kaye and Laby's tables (de Metz, 1890).

The density of the oil at several temperatures was determined by the weight-thermometer method, and the following results obtained:—

Density at 20° c. = 0·893 gm. per c.c.

Mean coefficient of expansion in range 0 to 100° c. = 0·00068.

Since, however, it is the ratio of the densities at 47° c. and 59° c. which is required, this is $1 - \frac{0{\cdot}00068 \times 12}{1} = 0{\cdot}992$.

Using the same method of calculation as used previously for water, we have

$$\text{Extension } E \text{ per unit volume} = \frac{1 - 3a(T-t) - D/d}{D/d} = 0{\cdot}0075.$$

$$\text{Tension} = E/e = \frac{0{\cdot}0075}{62 \times 10^{-6}} = 119 \text{ atmospheres.}$$

The above result has been obtained while avoiding rapid heating or cooling. It is thus evident that even when the ordinary Berthelot method is carried out with great care high results are still obtained.

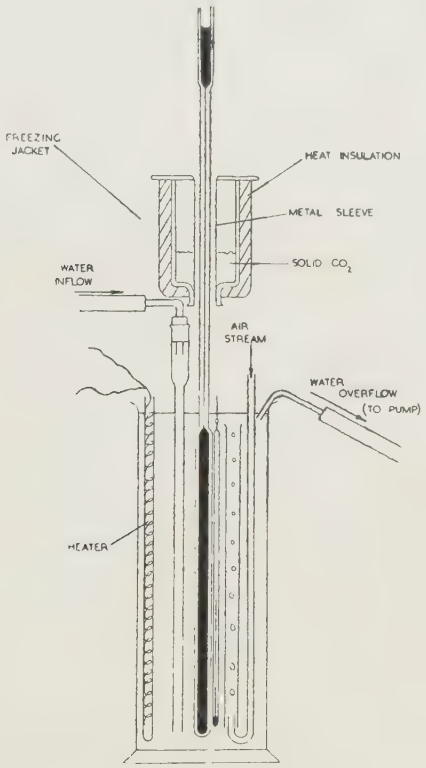
*Berthelot tube with alternative method of sealing*

A special Berthelot tube was constructed with a bulb consisting of 2-mm. wall capillary tubing with 2·5-mm. bore. The fine capillary had a bore of 0·2 mm. and the join between this and the bulb was strongly made, so that it would withstand considerable internal pressure. The instrument was filled with the mineral oil previously described, by the method already given.

The method of sealing the bulb was to freeze about 4 inches of the oil column in the capillary by surrounding it with solid $CO_2$. The apparatus is shown in the figure. The bulb was completely immersed in a bath of water which was vigorously stirred by a bubbling device. The bath was heated by an electric

immersion heater and allowed to cool naturally. The freezing jacket was made from a glass bottle with the bottom removed as shown, and the copper sleeve which was inserted in the cork and passed over the capillary stem of the Berthelot tube made it possible to slip off the freezing jacket when desired. The jacket was lagged and a lid provided to minimize inflow of heat.

To carry out a tension measurement by the Berthelot method, the bulb was heated to about 30° c. and kept at a steady temperature for about 15 minutes. The freezing jacket was then slipped over the fine capillary stem and a time of 5 minutes allowed for the oil therein to freeze and so produce a solid plug which completely sealed the bulb, the pressure within being atmospheric. By cooling the bulb, the pressure within falls; and, provided no break occurs, a state of tension is produced which increases until finally the tension is relieved by the




Special Berthelot tube.

formation of one or more cavities. If the bulb is heated after sealing, pressure is generated inside. When pressure was generated in this way, the capillary was unfrozen for a short time to allow the oil in the tube to get definitely to atmospheric pressure before re-sealing and cooling for tension measurements.

The temperature at which the capillary column was frozen is referred to as the sealing temperature, and the difference between this and the breaking temperature is called $\Delta T$.

Berthelot measurement

| Experiment | $\Delta T$° c. | Tension (atmo.) |
|---|---|---|
| No. 1 | 0·6 | 4·7 |
| ,, 2 | 0·1 | Nil |
| ,, 3 | 0·85 | 7·2 |
| ,, 4 | 1·0 | 8·7 |
| ,, 5 | 1·05 | 9·0 |
| ,, 6 | 2·5 | 23 |
| ,, 7 | 2·55 | 25 |

In experiments 1 to 3 the breaks were in the capillary, but in 4 to 7 the breaks were in the bulb.

In experiments 8 to 15, pressure was applied before tension measurements, as described above, and was adjusted to atmospheric prior to final sealing. The difference between the maximum temperature attained and the sealing temperature is given as $\Delta T_p$.

| Experiment | $\Delta T_p$° c. | Applied absolute pressure (atmo.) | $\Delta T$° c. | Tension (atmo.) |
|---|---|---|---|---|
| No. 8 | 1 | 10·6 | 0·7 | 5·7 |
| ,, 9 | 2 | 20·3 | 1·1 | 9·6 |
| ,, 10 | 3 | 29·9 | 2·65 | 24·5 |
| ,, 11 | 5 | 49·2 | 0·9 | 7·7 |
| ,, 12 | 10 | 97·3 | 0·4 | 2·8 |
| ,, 13 | 11·4 | 110·8 | 0·2 | 0·9 |
| ,, 14 | 6 | 58·8 | 0·7 | 5·8 |
| ,, 15 | 0·8 | 8·6 | 0·9 | 7·7 |

In experiments 8 to 15 all breaks occurred in the bulb.

## § 3. CONCLUSIONS

The experiments described show that the Berthelot method, when sealing by freezing is used, gives results which are more comparable with those obtained by the viscosity tonometer. Although a result as high as 25 atmospheres was obtained by the modified Berthelot method, there is no reason to think that an equally high value could not be obtained by the viscosity tonometer. It will be remembered that values up to 7·8 atmospheres have previously been reported (Vincent, 1943). It is concluded from the results of the modified Berthelot method that tensions up to 25 atmospheres can be produced in oil within a glass vessel, but the high values of over 100 atmospheres which can be obtained by the ordinary Berthelot method are regarded as false on account of the high pressure which is liable to exist at the moment of disappearance of the final bubble, and which is assumed to be zero when calculating the tension.

## ACKNOWLEDGEMENTS

Our thanks are due to Mr. I. K. Fisher, B.Sc., and to Mr. T. H. Staines for assistance in the experimental work, and to Callender's Cable and Construction Company for permission to publish this paper.

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# PHOTO-ELASTIC INVESTIGATIONS OF STRUCTURAL CHANGES IN PLASTIC MATERIALS

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*ABSTRACT.* The orientation and structural changes in four plastics—polythene, nylon, methyl methacrylate polymer, and polystyrene—resulting from the application of known stresses are investigated by measurements of the optical anisotropy induced. The mechanism of " cold-drawing " in the case of polythene and nylon is considered in detail and the birefringence correlated with the mechanical strain. The anomalous birefringence of polystyrene and methyl methacrylate is attributed to the orientation of side groups. Some investigations of the dependence of structural changes on temperature are also described.

## § 1. INTRODUCTION

Two methods are normally available for investigating the changes in behaviour of materials which take place when they are strained. An investigation of their mechanical properties, stress-strain and flow curves gives an indication of the variation in external form, whilst x-ray investigations yield data on the changes in the ultimate atomic arrangement. When the material is comparatively transparent, a third method is available, namely, that of observing birefringence induced by strain. The information obtained by this method may be considered as intermediate between that found with the microscopic and macroscopic techniques.

This optical technique gives a measure of the anisotropy produced in the structural arrangement of transparent materials when they are strained under the influence of external stresses. It also gives the average departure from an isotropic arrangement, whether regular atomic arrays are present in the substance or not, and, therefore, has the advantage that it can be applied to amorphous substances, where the degree of orientation is too small to be observed by x-ray diffraction methods. Treloar (1941) has discussed the effect of orientation on the birefringence produced by the rotation of crystals along the direction of stretching, and has shown that the increase in birefringence becomes smaller as complete orientation is approached. Amongst the published work in this field, several investigations have been made on rubber (Bjerken, 1891; van Geel and Eymers, 1929; Treloar, 1941), cellulose sheets (Spence, 1941), and the work on some plastic materials has been discussed by Houwink (1934).

## § 2. EXPERIMENTAL

The experimental arrangement used is shown in figure 1. A parallel beam of plane-polarized monochromatic light, obtained from a mercury arc with a green filter ($\lambda = 5461$ A.), is passed through the specimen, the plane of polarization making an angle of 45° with the direction of strain. The optical path difference

of the vertical and horizontal plane-polarized components of the emergent light gives the difference in the values of the refractive indices. A travelling microscope was used to measure the displacement of the system of interference fringes obtained with a Babinet compensator.

The specimens were in the form of thin rectangular sheets clamped at each end between small metallic plates, loads being applied on a scale-pan suspended from the lower plates. In order to maintain the specimen at higher temperatures, a constant temperature enclosure was employed. The enclosure was heated electrically and could be raised to about 150° C. by means of a rheostat, the temperature being measured by a thermometer. Care was taken to ensure that the compensator remained at the same temperature throughout, as the optical properties of quartz vary with the temperature, leading to incorrect values of the fringe shift.

White light obtained from a Pointolite source was used to determine the central fringe in each case, giving the integral number of wave-lengths, accurate

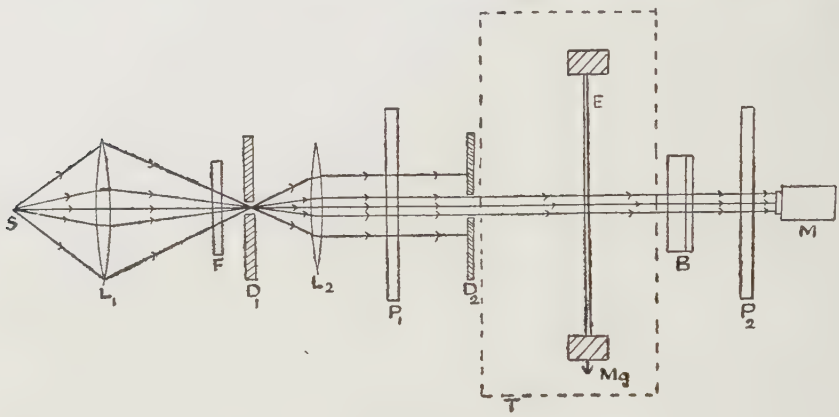



Figure 1. Experimental arrangement.

S=source, $L_1L_2$=lenses, F=filter, $D_1D_2$=diaphragms, $P_1P_2$=polaroid screens, E=specimen B=Babinet compensator, M=travelling microscope, T=constant temperature enclosure.

measurements then being taken with the monochromatic light. As a result of the difference between the relative dispersive powers of the plastic and quartz, the central fringe with white light becomes coloured for shifts of more than about eight wave-lengths, and preliminary experiments were made to allow for this effect. The second settings for large shifts were made on a fringe near the centre of the compensator, ensuring that the light had passed through the central portion of the specimen.

If $c_p$, $c_q$ are the velocities of the light through the material polarized in two directions at right angles, $\boldsymbol{c}$ the velocity *in vacuo*, then the path difference $p$ for a specimen of thickness $d$ is given by

$$p = d\left(\frac{1}{c_p} - \frac{1}{c_q}\right)\boldsymbol{c},$$

$$p = d(n_p - n_q)$$

(where $n_p$ and $n_q$ are the corresponding refractive indices)

$$\text{or} \qquad \Delta n = p/d.$$

For most materials it is found that for small stresses $\Delta n$ is proportional to the applied stress, the linear relation being known as Brewster's Law. Coker and Filon (1931) have defined a unit, called the *brewster*, which is $10^{13}$ times the constant of proportionality between the dimensionless number $\Delta n$ and the applied stress measured in dynes/cm$^2$.

Varying loads were applied to the specimen, and the true values of the stress were found for each observation by accurately measuring the actual breadth and thickness in the region through which the light passed. The travelling microscope enabled the path difference to be measured to about 1/100 wavelength; for a specimen 0·5 mm. in thickness this corresponds to an accuracy of about $1 \times 10^{-4}$ in the value of $\Delta n$. Several settings were made for each value of the applied stress, and several hundred readings in all were thus taken for each curve.

## § 3. POLYTHENE AND NYLON

Bunn (1941) studied the structure of polythene (polymerized ethylene) by x rays. He has obtained polycrystalline diffraction patterns which reveal that the crystal size is considerably smaller than the chain length. Hence the structure would appear to consist of crystalline groupings each of which is made up of portions of the molecular chains of sufficient extent in three dimensions to give sharp diffraction phenomena. The substance is wax-like in appearance and

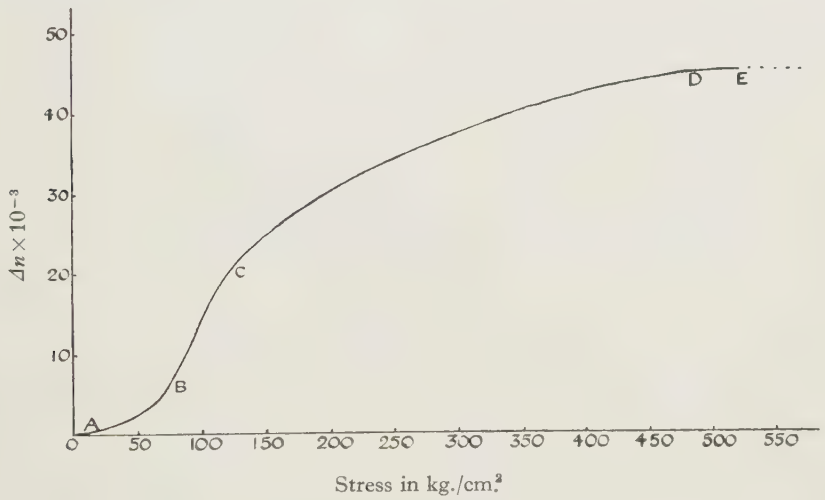


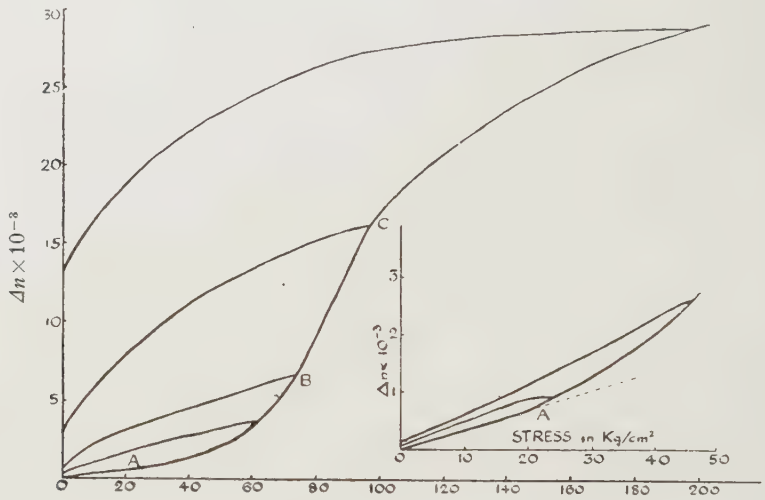

Figure 2. Polythene stress-birefringence curve at 20° c.

cold-draws readily, its length increasing four-fold, and then resists further extension.

A number of specimens, from sheets prepared in several ways, from a standard polythene (i.e. of one molecular-weight distribution), which showed no initial optical anisotropy in the plane of the sheets, were examined; due to the partial opacity a limit of 1 mm. was placed on the thickness which could be readily employed. The general nature of the {stress, birefringence} curve at 20° c. is shown in figure 2; the lower portion, including hysteresis effects, is shown on a large scale in figure 3. These curves may be conveniently divided

into five separate sections. For comparatively small stresses up to about 20 kg./cm.$^2$ (point A), the birefringence is directly proportional to the applied stress and disappears entirely on removal of the load (see inset, figure 3). Brewster's law is thus obeyed in this region, giving a value for the stress-optical coefficient of about 260 brewsters (cf. glass 0–10; rubber 2000).

The rate of change of the birefringence with the stress increases fairly rapidly for greater applied stresses and reaches a maximum value at a stress of about 80 kg./cm.$^2$ (point B). At these higher stresses there was some time flow. In the third section of the curve, from B to C (100 kg./cm.$^2$) the birefringence increases at a fairly uniform rate which is about eighteen times that in the linear portion OA. In this section of the curve the fringes were observed to become rather ill-defined, indicating that the distribution of the strain was not uniform over the portion of the specimen examined. This effect may be due to the




Stress in kg./cm.$^2$

Figure 3. Polythene stress-birefringence curve.

non-uniform orientation of the micelles just before the region of cold-drawing. The fringes once again became sharp when higher stresses were applied.

Beyond C, the rate of change of birefringence with stress decreases, but the length of the specimen increases rapidly, the region corresponding to the process of cold-drawing. At a stress of about 500 kg./cm.$^2$ (point D) cold-drawing is completed and the application of higher loads results in very little increase in either the length or birefringence of the specimen. The fifth portion of the curve (beyond D) is thus appreciably flat up to the breaking stress E.

No hysteresis effects were observed in the linear region (OA), but for higher stresses the hysteresis effects were fairly great, the residual birefringence decreasing most rapidly as the load approached zero, large residual strains being found. After the specimen had been cold-drawn, decreasing the load had very little effect on the optical strain, the residual strain when the load had been removed being almost as great as that at the load after cold-drawing.

Similar investigations were carried out with nylon (a polyamide), of which the mechanical behaviour and structural arrangement are somewhat similar to polythene. The curve obtained for the change in birefringence with applied stress is shown in figure 4, a curve for polythene on the same scale being included for comparison. It can be seen that the general nature of the curve is similar to that found for polythene, and consists of a short linear portion (OA), a rapid rise (BC) and then a flat portion (DE), where no appreciable change in birefringence with load is detected. The lower portion of the curve with typical hysteresis loops is given in figure 5. The gradient in the linear portion is not so great as for polythene—the stress-optical coefficient amounts to about 100 brewsters—but it is more extensive, and departs from linearity after a stress of 110 kg./cm.$^2$ (A) has been reached. A slight amount of time flow was observed even for these small values, but the birefringence reached a constant value after the load had been applied for a few minutes.

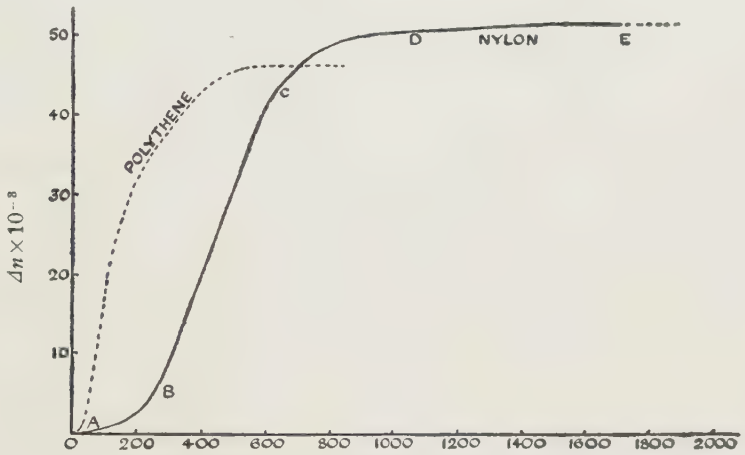



Figure 4. Nylon stress-birefringence curve at 20° C.

In the second section, AB, the increase of birefringence becomes more and more rapid until it reaches a uniform rate at a stress of about 230 kg./cm.$^2$ This uniform rate of increase continues up to a stress of 700 kg./cm.$^2$ (C), and although the value of the gradient is less than that for polythene, the value of the birefringence at the point of inflection is greater than the corresponding values on the polythene curve. The decrease in definition of the fringes was noticed in this region as for polythene, but on further increasing the applied stress they again became quite sharp. The gradient decreases continually in the fourth section of the curve, and at a stress of about 1100 kg./cm.$^2$ (D) the cold-drawing has been completed, and the addition of further loads causes very little increase in the birefringence. The final flat portion of the curve (DE) continues up to the breaking point, which was found to be of the order of 2000 kg./cm.$^2$ (E), which is considerably less than for nylon fibres.

In the linear portion, the upward curve is retraced fairly closely on reducing the load. At an applied stress of 200 kg./cm.$^2$ it can be seen that the return

curve follows a path roughly parallel to that of the ascending curve down to about 10 kg./cm$^2$, when the optical strain is equal to about one-third of its original value; but on further reducing the load there is a sharp drop in the birefringence, and only a small residual strain can be detected when the load is completely removed. For higher initial loads the curves are similar to the one described above, but the fall in birefringence is less sharp for small residual loads. The hysteresis curves obtained after the specimen has been cold-drawn are flatter than with undrawn specimens, but not so flat as the corresponding curves for polythene. The small change observed on unloading cold-drawn specimens is, however, quite reversible, and corresponds to the elastic behaviour of nylon in the cold-drawn state. The application of stresses of about

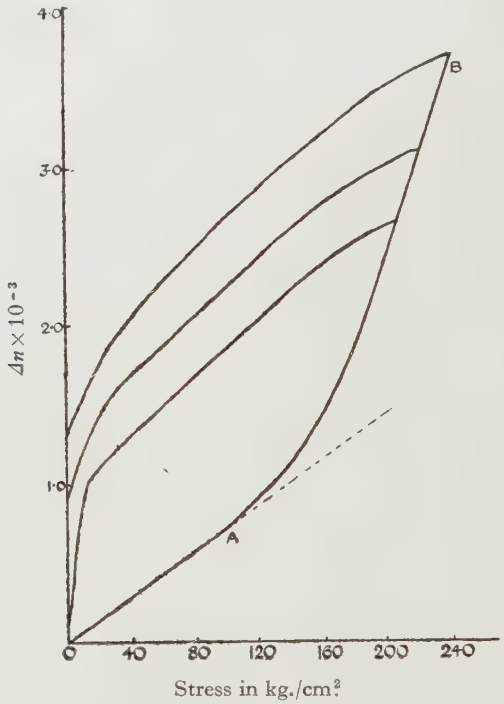



Figure 5. Nylon stress-birefringence curve.

200 kg./cm$^2$ at 20° c. would appear to deform the material to a critical state, in that the restoring forces are just able to overcome the deformation when the stress is removed. Any further increase of the stress, however, produces large permanent strains.

A comparison between the stress-birefringence curves for polythene and nylon (figure 4) shows that in the completely cold-drawn state both substances have approximately the same birefringence, and if the degree of orientation in the two substances is about the same, the inherent optical anisotropy of the individual crystalline micelles must be approximately equal.

It was found inconvenient to make accurate observations of the mechanical strain simultaneously with the optical strain, and so the experiments were repeated under the same conditions, measuring the variation of mechanical

strain with stress. Curves were then obtained for the mechanical strain against optical strain at various applied stresses (figure 6).

In both cases a linear relation exists well above the elastic limit up to an extension of about 35% of the original length, when the applied stress in the case of polythene is about 100 kg./cm$^2$, whilst in the case of nylon it is about 500 kg./cm$^2$. For nylon it can be seen that it has acquired almost its maximum birefringence at an extension of 100%, whilst in polythene there is a steady increase in the birefringence up to the breaking point.

In the linear region the stretching must consist mainly of the orientation of the crystalline micellar units, for both materials. The steeper gradient of the nylon curve would appear to indicate that the forces resisting lateral motion between micelles are greater than those hindering rotation, and this may be attributed to the presence of cross-affinities between molecular chains, which are absent in polythene.

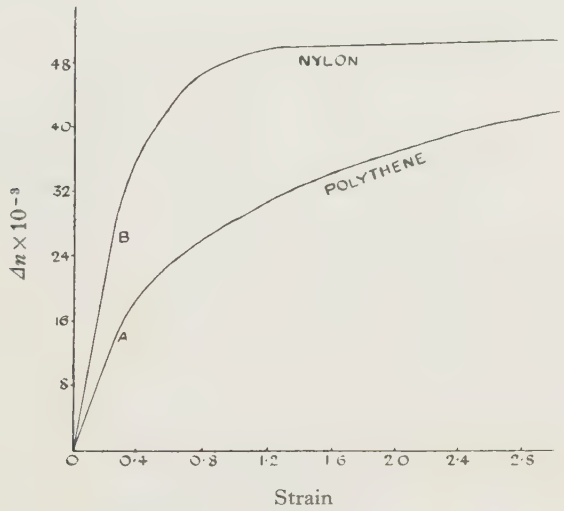



Figure 6. Strain-birefringence curves.

The flattening of the curve at higher elongations may be attributed partly to the high degree of orientation, so that the changes in optical strain are small, and partly to the gliding re-arrangement of the crystalline micellar units which occurs during cold-drawing. The difference between polythene and nylon in this case may be due to the presence of strongly polar carbonyl groups in the latter, as the position of the double-bonded C=O groups relative to the chain will modify the optical characteristics of the material.

The possibility of the formation of new crystalline groupings from the amorphous matter constituting the "tie-molecules" during cold-drawing can be seen from the shape of the curves beyond 100% elongation. It would appear unlikely that this would occur in the case of nylon, where there is no further increase in birefringence, but that it may be possible with polythene.

In order to study the optical behaviour at higher temperatures the electrically heated enclosure was employed, the experimental procedure being otherwise the same as at room temperature. The {stress, birefringence} curves obtained

in this way for specimens of polythene at various temperatures are shown in figure 7. The general nature of the curves is seen to be the same in all cases, but for a given applied stress the birefringence increases with the temperature.

The nature of the structural changes, in the range considered (20–90° c.), which occur during stretching do not appear to be altered by an increase in the temperature of the specimens, but since at higher temperatures the mobility of the molecules is greater, both the orientation of micelles and the process of cold-drawing take place at much lower values of the applied stress. The value of the birefringence after cold-drawing was found to be the same at all temperatures, and did not increase appreciably when further loads were applied to the cold-drawn specimens. The value of the breaking stress was, however, found to be lower at the higher temperatures.

Figure 8 shows a series of curves obtained with polythene for the variation of birefringence with temperature for a constant applied stress. The stress

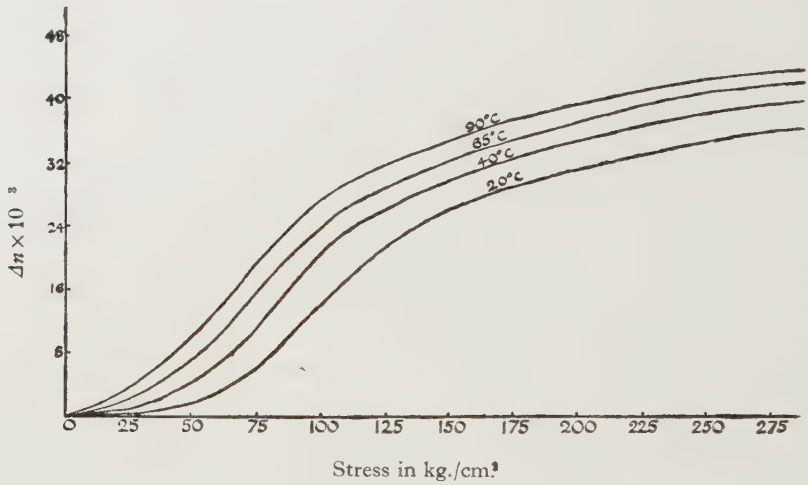



Figure 7. Stress-birefringence curves for polythene at different temperatures.

was maintained at a constant value by decreasing the load as the breadth and thickness decreased. It can be seen that for stresses below about 20 kg./cm.² the birefringence increases very slowly up to a temperature of about 80° c. and then rises fairly rapidly. As the value of the applied stress increases, the temperature at which this rapid rise takes place becomes lower, and the rate of change of birefringence becomes greater. Above a stress of about 60 kg./cm.² a rapid uniform rise takes place as the temperature is increased and continues until the cold-drawing of the specimen takes place.

These investigations of the change in birefringence with temperature at a constant stress cover the portion of the {stress, birefringence} curve where the birefringence is rapidly increasing with the stress, but as no correspondingly large increase in the strain takes place, the process must be largely one of orientation of the constituent structural units. The thermal agitation of the molecules increases with rise in temperature and, for each value of the applied stress, there is a temperature at which the combined effect of this agitation and the applied

stress is just sufficient to balance the intermicellar forces opposing orientation. A slight increase in the temperature will then produce a large increase in the orientation along the direction of the applied stress. The curves show that at low values of the stress, this rapid increase of birefringence with temperature commences just above 80° c. (at which temperature the material softens), whilst for stresses above 60 kg./cm.$^2$ the thermal agitation at room temperatures is sufficient for the orientation to increase rapidly with further increase in temperature.

The residual strain in unloaded specimens is lowered at higher temperatures by the increased mobility of the molecules. Figure 9 shows the effect of increasing the temperature of a specimen which had a large residual strain, the value of which ($\Delta n = 3{\cdot}3 \times 10^{-3}$) corresponded to the strain left after a load of

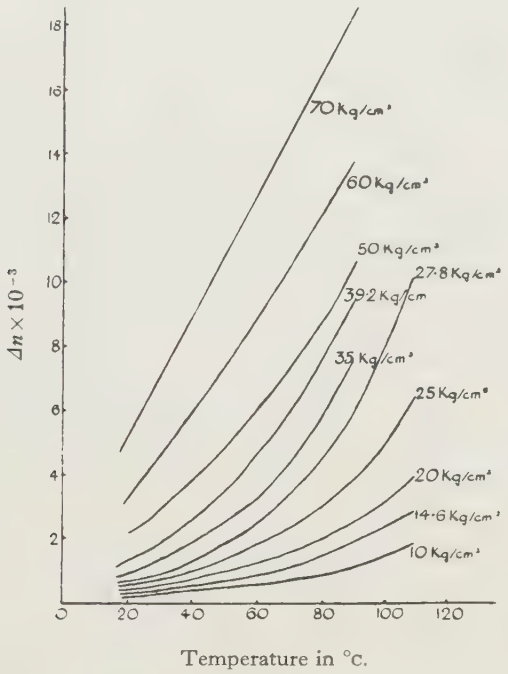



Figure 8. Polythene temperature curves at constant loads.

100 kg./cm.$^2$ had been applied at room temperature. The strain fell to about $0{\cdot}5 \times 10^{-3}$ (point B) when the temperature was raised to 110° c., the fall being most rapid during the last fifty degrees. When the temperature was again lowered to 20° c., the birefringence rose to about $0{\cdot}9 \times 10^{-3}$, the portion BC of the curve being retraceable by varying the temperature from 20° to 110° c.

The large fall in the birefringence from A to B corresponds to an irreversible random re-orientation of the molecular groupings under the influence of thermal agitation. On cooling, some of the vibrations still take place about a mean position along the direction of strain, and orientation takes place along this direction, giving rise to the small birefringence (C) detected. The process is reversible, and is solely dependent on the temperature and the degree of original orientation under stress.

Some observations were made of the photo-elasticity of nylon at temperatures up to about 100° c. There was very little difference in the nature of the curves obtained at the various temperatures, but for a given applied stress, the value

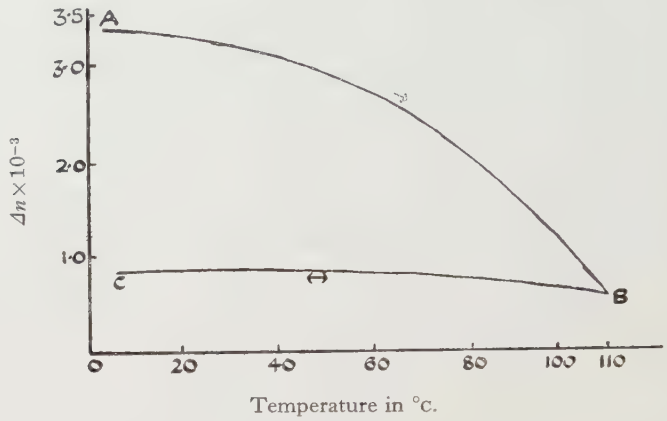



Figure 9. Polythene temperature cycle.

of the birefringence was found to increase on heating, and the sharp uniform rise in the central portion of the curve was also found to be steeper at the higher temperatures.

## §4. METHYL METHACRYLATE POLYMER AND POLYSTYRENE

The specimens of methyl methacrylate polymer examined were in the form of sheets of about 1 mm. thickness and, since these contained a percentage of plasticizer, the photo-elastic behaviour may have been modified slightly. On applying even comparatively large loads, at room temperature, only a very slight negative birefringence was observed. On heating the specimens, measurable values were obtained, but the induced birefringence was always negative and the nature of the phenomenon was rather more complex than that observed with polythene and nylon.

The value of the refractive index for plane-polarized light in a substance depends on the electrical polarizability of the constituent groups in the direction of the plane of the electrical vector of the polarized light. When most materials are strained, the refractive index for light polarized along the direction of stretching increases, as a result of the molecular groups becoming aligned, so that their dipole moments along the direction of stretching are greater than those at right angles to it. This is found to be the case for most glasses, celluloid, bakelite, rubber, polythene, etc. The anomalous effects observed with methyl methacrylate and polystyrene must be attributed to the orientation of the side groups in the molecular chains at right angles to the chain itself, and the effect of these side groups must more than counterbalance the effect of the carbon chain alone.

Figure 10 shows the behaviour of a specimen of polymethyl methacrylate under a load of 160 kg./cm² when the temperature was varied. On first applying the load at 20° c. only a very slight birefringence could be observed (A), but on

raising the temperature this increased, and at 90° c. the value $\Delta n$ was $-0{\cdot}8 \times 10^{-3}$ (B). When the specimen was cooled, the load still being applied, the value rose further to $-4{\cdot}2 \times 10^{-3}$ at 20° c. (C), and removing the load at this temperature made no appreciable difference to the birefringence. When the unloaded specimen was again heated, this residual optical strain decreased, and at a temperature of 90° c. (D) had completely disappeared, but cooling the specimen produced a birefringence which increased until it reached a value of $-1{\cdot}8 \times 10^{-3}$ at 20° c. (E). This latter portion of the curve DE was found to be quite reversible, and could be retraced in either direction by varying the temperature between 20° and 90° c.

The effects observed with methyl methacrylate polymer must be attributed to the behaviour of the strongly polar carbo-methoxy side groups on heating and stretching the specimen. In the first section of the curve (AB) when the

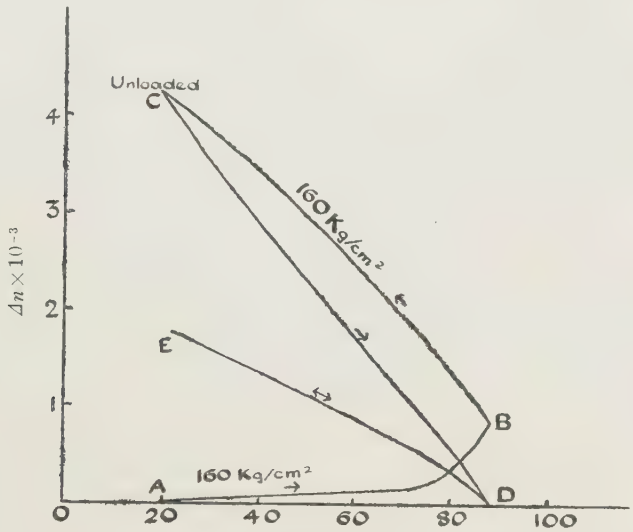



Figure 10. Methyl methacrylate polymer temperature cycle.

specimen is heated under load, a partial drawing out of the sections of the molecular chains takes place along the direction of stress, and some side groups become aligned perpendicular to this direction. As a result of thermal agitation, however, these groups are vibrating about mean positions around the single bond and do not have their full effect on the optical anisotropy. When the specimen is cooled under load (BC), these vibrations decrease in amplitude and the value of the birefringence increases. Decreasing the temperature also lowers the mobility of the molecules as a whole, and when the load is now removed (C) the structural arrangement remains unchanged.

If the unloaded specimen is now again heated, the thermal motion causes the molecular arrangement to become random, and at a temperature of 90° c. the positive birefringence of the main chain just neutralizes the effect of the vibrating side groups, so that no optical anisotropy could be observed (D). On once again cooling the specimen under no load, the vibrations of the side

groups decrease and a negative birefringence can be observed (E). Subsequent heating of the specimen just changes the amplitude of the vibration of the group and is therefore quite reversible. This reversible portion of the curve is similar to that found with polythene (figure 9), but the effect was there much smaller in magnitude.

Although the x-ray patterns of stretched polystyrene (Katz, 1936) show equatorial maxima corresponding to the spacings between adjacent chains, there is no evidence of orientation in the other haloes corresponding to the identity period along the chain, and it therefore seems likely from this and the optical behaviour of the material that only small sections become aligned and orient the side groups accordingly. Polystyrene, like methyl methacrylate, shows very little photo-elasticity at room temperatures, but on heating under load, considerable negative birefringence remains. Signer (1936) has considered this negative birefringence in polystyrene solutions and has pointed out that the benzene ring must not only be oriented with its axis at right angles to the chain, but its plane must also be perpendicular to the plane of the chain. The polarizability in the plane of the ring is twice that in a direction at right angles to it, so that an anisotropy will be present in the polystyrene chain which will completely dominate that of the carbon chain, which is in the opposite direction.

## § 5. CONCLUSION

The photo-elastic investigations of these plastics, when taken in conjunction with the mechanical and x-ray data available, have revealed considerable information of the nature of the structural changes which take place on stretching. They have also given quantitative values of the stresses and temperatures at which the various structural processes take place and have revealed the effects of increasing the temperatures of the specimens.

From x-ray evidence it is found convenient to divide plastic materials into three groups: those which are already crystalline, those which become crystalline on stretching and those which remain amorphous. Polythene and nylon belong to the first group and give a polycrystalline x-ray diffraction pattern, but as a result of the long-chain structure of the molecules, the crystals cannot be considered to have any separate existence, and consist of small micellar groupings, composed of sections of a large number of molecular chains. Substances of this type generally show a large positive birefringence on stretching, and the small increase during cold-drawing would appear to indicate that a gliding re-arrangement of the crystalline micellar groupings takes place in this region, whilst it may be possible for new crystalline groupings to be formed from the "tie-molecules". Small further extensions after cold-drawing can only take place by overcoming the strong primary binding forces between atoms in the molecular chains. The internal forces at right angles to the chains would therefore be expected to be in the nature of secondary attractions between adjacent chains, as is borne out by the much lower strength of the specimens in this direction.

The second group, which includes natural rubber, polymerized dimethyl butadiene and polyisobutylene, give amorphous x-ray patterns when they are

unstretched, but sharp x-ray patterns are obtainable on stretching. No photo-elastic measurements have yet been made with a material of this type in these investigations, but from the work of Treloar it is seen that natural rubber has a large positive birefringence when stretched.

The other two plastics considered—methyl methacrylate polymer and polystyrene—fall into the third group, for which the arrangement of the molecules is quite random, and x-ray data alone give little information on the effect of stretching on the structural arrangement. The photo-elastic investigations on these substances have, however, indicated that small sections of the chains become aligned along the direction of stretching and orient the side groups accordingly. Increasing the temperature of the specimens has been seen to decrease the extent of this orientation as a result of the thermal agitation causing vibration of these side groups.

## § 6. ACKNOWLEDGEMENTS

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# EXPERIMENTAL STUDY OF THE INTENSITY THEORIES IN BAND SPECTRA: I, HUTCHISSON'S THEORY; II, LANGSTROTH'S THEORY

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## Part I. HUTCHISSON'S THEORY

*ABSTRACT.* The Second Positive system of $N_2$ was excited in a wide-bore discharge tube of the H-type by means of an induction coil, the primary supply for which was 10 volts at 1·5 amp. ; no spark gap or condenser was included in the secondary circuit. Integrated intensity values for all the measurable bands of the system were determined by photographic photometry. Transition probabilities for bands in emission are calculated from known molecular constants, with the help of the formula suggested by Hutchisson. Observed $I/\nu^4$ values (where $I$ is the integrated intensity) for bands belonging to different $v''$-progressions are compared with the calculated emission-probabilities, and it is found that the agreement is not satisfactory. The agreement is considerably improved by interchanging the vibrational quantum numbers.

Some of the factors responsible for the apparent failure of the theoretical treatment are discussed, and a probable reason for the improvement in agreement between the observed and calculated values on interchange of $v'$ and $v''$ is suggested.

### § 1. INTRODUCTION

Hutchisson (1930) has shown that wave-mechanical treatment permits the calculations of transition probabilities from the initial to the final state in absorption as well as in emission band systems of symmetric diatomic molecules. Moreover, Dunham (1930) has pointed out that, since the electric moment does not change nearly as rapidly as the eigenfunctions, Hutchisson's formula can be applied quite generally and need not be restricted to symmetric molecules and small quantum numbers only.

In absorption bands, where the distribution among the vibrational levels of the initial (lower) state can be calculated from the known temperature of the gas or vapour, this knowledge of the transition probabilities leads to the prediction of the relative intensities of the bands of an entire system. This, however, is not possible in the case of emission bands, where the distribution among the vibrational levels of the initial (upper) state is generally unknown; for it depends not only on the temperature but also on the method of excitation and upon whether or not the molecules have reached the initial excited levels by means of transitions from a higher level. Hutchisson's treatment thus permits the calculation of the relative intensities only of those bands of an emission system which originate from the same initial vibrational level. Hence, in emission, the intensity values calculated according to Hutchisson's methods and arranged

in the usual $v'$, $v''$ scheme, are expected to show agreement with the observed values of $I/\nu^4$ only along the $v''$-progressions.

A further development of this theory by Langstroth (1934, 35) suggests a method of calculating the relative intensities among the entire bands of an emission system under certain excitation conditions. In Part II of this paper we study this theory in the light of our results. Here only Hutchisson's theory is considered.

Hutchisson himself tested the validity of his theory in the light of experimental results obtained by others, mainly in the case of a few absorption systems, and one emission system, viz. the $3\,^1B \rightarrow 2\,^1S$ system of $H_2$. Most of the experimental results employed, however, were not obtained by the rigorous methods of photographic photometry.

Langstroth (1934, 35) determined the relative intensities of the Second Positive system of the $N_2$ molecule, and obtained far more accurate data for this system by the methods of photographic photometry. His work, which covered fifteen bands of the system, revealed that the agreement between the observed and calculated results was only approximate. Langstroth also refers to Tawde's (1934) experimental results on the same system; he observes that Tawde's work, which covers many excitation conditions, is particularly suitable for examining these theories, and that, even along $v''$-progressions, Tawde's results are not in accord with the relative intensities calculated from wave mechanics. This evidence cannot, however, be taken as a failure of the theoretical treatment, since Tawde's results, like most of those given by Langstroth, were peak intensity values; unless peak values are shown to be proportional to the integrated band intensities, one cannot draw from knowledge of the former any conclusions regarding the fundamental basis of the intensity theories. Tawde and Patankar (1940) have shown that, at least in the $N_2$ Second Positive system, integrated and peak values are not proportional. The collection of sufficient material, free from defects of the type mentioned above, which can unreservedly be considered valid for comparison with theoretical results is, therefore, essential for any further advance.

The present work is devoted to the detailed theoretical and experimental investigation of the band intensities of the $N_2$ Second Positive system. This system, which contains a large number of bands besides those examined by Langstroth, is particularly suitable for such an examination in view of Tawde's 1934 results, and of some of the disputable points to which Langstroth refers. Further reasons for the choice of this system are the ease with which the system can be excited and the absence of overlapping between most of the adjacent bands.

## § 2. THEORETICAL

Hutchisson (1930) has shown in detail how an expression can be developed which allows the matrix elements of the electric moments to be calculated for vibration transitions in symmetric diatomic molecules. The expression is

$$P_{n'n''} = C_3 \frac{(n'!\,n''!)^{\frac{1}{2}}}{2^{(n'+n'')/2}} \sum_{l=0}^{n' \text{ or } n''} \sum_{i=0}^{(n'-l)/2\ (n'-l-1)/2} \sum_{j=0}^{(n''-l)/2\ (n''-l-1)/2} a_{2l}\, b_{2i}\, c_{2j}\, d_{n'-2i-l}\, e_{n''-2j-l}. \qquad \ldots\ldots (1)$$

Full details about the various terms in this expression are given in Hutchisson's paper. Squaring it gives the transition probability between the vibrational levels $n'$ and $n''$ (or $v'$ and $v''$). The relative intensities of bands in the electronic-vibration spectra of symmetric diatomic molecules can then be calculated as the products of $(P_{n'n''})^2$ or $(P_{v'v''})^2$, the fourth power of the frequency of the band-head ($\nu$), and the distribution factor of the molecules in the initial state. However, as pointed out earlier, the distribution factor for the initial state being generally unknown for emission systems, it is only possible in these cases to calculate the relative intensities of those bands which originate from the same initial level.

The quantities $a$, $b$, $c$, $d$, and $e$ in expression (1) are functions of $\alpha$ and $\delta$, where

$$\alpha = (\nu_0''/\nu_0')^{\frac{1}{2}},$$
$$\delta = 0{\cdot}1221(r_0' - r_0'')(\nu_0'' M)^{\frac{1}{2}}.$$

For the calculation of the transition probabilities, a knowledge of the values of $r_0'$ and $r_0''$ (the distances between the atomic nuclei in the equilibrium positions) and $\nu_0'$ and $\nu_0''$ (the frequencies of vibrations) for the initial and final electronic states is necessary. In calculating his results, Langstroth (1934, 35) has taken the values for these quantities for the $C^3\Pi$ and $B^3\Pi$ states of the neutral $N_2$ molecule from the International Critical Tables (1929). For our calculations we have taken values from Jevons' *Report* (1932), a more recent publication. As there is some disparity in the values of these quantities as given in the two sources, it was deemed necessary to use the revised values in our calculations. The values of transition probabilities in emission calculated in this way are given in table 1.

## § 3. EXPERIMENTAL

Using a step-slit, the relative intensities of the $N_2$ Second Positive system were measured accurately by photographic photometry. The principles and the details of the technique are given by Read and Johnson (1931). More recently, Johnson and Tawde (1932), Elliott (1933), and Elliott and Cameron (1934) have given improved methods of photographic photometry as applied to band spectra. The bands were excited in a discharge tube of the usual H-type with aluminium electrodes, the central part being 25 cm. long and having an internal diameter of 0·7 cm. All the glass tubing used was thoroughly cleaned. Two small bulbs filled with $P_2O_5$ and KOH were attached to the discharge tube.

For each exposure, the discharge tube was filled with pure dry nitrogen, and the pressure was adjusted to 1·2 mm. Proper precautions were taken to prevent any mercury vapour from the manometer from entering the discharge tube. The discharge was run by an induction coil giving a high-frequency voltage. No condenser or spark gap was used in the circuit. The primary voltage and current were 10 v. and 1·5 amp. respectively. The current in the secondary was 1·0 ma. By proper adjustment the current in the discharge tube was never allowed to vary by more than $\pm 0{\cdot}10$ ma.

The standard lamp used in these investigations was of a special type and was supplied by the General Electric Company. It was of u.v. glass, with a small spiral filament of tungsten. The lamp was calibrated by Johnson and Tawde at the Government Chemical Laboratory, London, and the data supplied to us

through their courtesy have been used here. The lamp current, during the exposure, was maintained strictly constant at 1·9 amp., the value at which it was calibrated.

The bands were examined end-on through the quartz window of the discharge tube, and were photographed on an R. Fuess quartz spectrograph and a Hilger glass-prism infra-red spectrograph, the former having a dispersion of about 13 A. per mm. at 3000 A. and 46 A. at 4600 A., the latter having a dispersion of 11 A. and 44 A. per mm. at 4200 A. and 6000 A. respectively. With each instrument the slit was adjusted to a value which just made the fine structure of the bands disappear.

Ilford Rapid Process Panchromatic plates were used, and the exposed plates were developed immediately after exposure, since, as pointed out by Keenan (1931), any lapse of time between exposure and development results in a change in the optical density on the plate. The development was carried out in absolute darkness under standard conditions. The developer and fixing-bath solutions were prepared afresh each time according to instructions supplied with the plates. In order to ensure that the development was uniform all over the plate, and to reduce the well-known Eberhard effect, a swirling device was used consisting of a wooden partition which moves backward and forward in the developing dish and causes an extremely turbulent flow of the developer on the plate. The plates were developed, fixed and washed at 65° F., to avoid frilling and fogging.

On each plate two sets of spectra and calibrating marks were taken, one for a group of strong bands and another for a weaker group. Intensities from one group to another were correlated by means of bands of intermediate intensities, which were measurable on both sets. The times of exposure for the calibration marks and the accompanying spectrum were kept strictly equal, and were such that the spectrum blackenings were intermediate between the maximum and minimum blackenings of the comparison calibration marks. In order to get comparable optical densities from the standard lamp and the discharge tube, with equal times of exposure, either a suitable number of neutral filters were inserted before the former, or the distance from the spectrograph was suitably varied.

Of the several plates taken in the manner described above, only a few were selected for getting the microphotometer records. Several microphotometer records were taken on a Kipp and Zonen self-recording instrument, which was tested initially for perfect reproducibility. Characteristic {blackening, intensity} curves were prepared for each band for each separate exposure on each plate under examination.

In cases where the overlapping of successive bands or the disturbing effect of foreign lines is practically absent, the most accurate method, free from any objections, is that of *total integrated intensities*. We have followed this method for estimating the relative band-intensities. Actually, microphotometer records of the calibration marks were taken only against the heads of the various bands. Since, however, in the integration method, intensities at various points inside the band are to be computed, and since the plate sensitivity varies rapidly in certain regions, the intensities at various points inside a band were calculated, not from only one {blackening, intensity} curve corresponding to the band-head, but

two or three more such curves drawn by extrapolation. Peak intensities were also evaluated for the purposes of comparison with the integrated intensities.

Since, in the method of integrated intensities, we plotted the intensities corresponding to different points on the microphotometer record against the distance along the record, it was necessary to apply a correction for dispersion. The relative intensities of the bands of the $N_2$ Second Positive system, after correction for the energy distribution of the standard lamp, were finally expressed relative to the (0, 0) band as 1000. In this type of work there is no need to apply the correction for reflection and absorption losses in the spectrograph, since they are common to the spectrum and the calibration marks and do not cause any errors in the relative intensity measurements.

Despite all the precautions taken, no claim to very great accuracy can be made. This is evident from the very difficult nature of photometric work of this type, involving a number of processes which cannot be very well controlled. Our difficulties were increased also on account of the extensive spectral region under investigation. The accuracy attained for the different bands is different. The error lies within the limits of 10 to 12%.

## § 4. RESULTS

The values of the transition probabilities in emission calculated with the help of Hutchisson's formula are given in table 1. For comparison, the values, as calculated by Langstroth (1934, 35) with the help of constants given in the International Critical Tables, are entered in brackets below our calculated

Table 1. Emission probabilities ($P^2_{v'v''}$) calculated by Hutchisson's formula

| $v'$ \ $v''$ | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| 0 | 1·000<br>(1·000) | 0·789<br>(0·835) | 0·249<br>(0·278) | 0·038<br>(0·047) | 0·003<br>(0·004) |
| 1 | 0·669<br>(0·704) | 0·073<br>(0·057) | 0·711<br>(0·704) | 0·491<br>(0·522) | 0·122<br>(0·148) |
| 2 | 0·282<br>(0·313) | 0·463<br>(0·046) | 0·036<br>(0·059) | 0·409<br>(0·365) | 0·621<br>(0·652) |
| 3 | 0·093<br>— | 0·416<br>— | 0·166<br>— | 0·194<br>— | 0·146<br>— |
| 4 | 0·027<br>— | 0·216<br>— | 0·369<br>— | 0·016<br>— | 0·290<br>— |
| 5 | 0·007<br>— | 0·084<br>— | —<br>— | —<br>— | —<br>— |

values. The agreement is fairly close in most cases. The only marked disagreement is in the values of the 2, 1 band; Langstroth's extremely low value for this band is evidently due to an error in the decimal point.

The values of transition probabilities, calculated by us, have been taken for comparison with the observed values of $I/\nu^4$, which are recorded in table 2. The

values of $I$ used in table 2 are the integrated intensity values determined in the way already described, while the denominator $\nu^4$ for each separate band is obtained from the frequency $\nu$ for the band-head, calculated from the band-head equation for the $N_2$ Second Positive system given in Jevons' *Report* (1932).

Table 2. Observed values of $I/\nu^4$

| $v'$ \ $v''$ | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| 0 | 1·000 | 0·750 | 0·365 | 0·166 | 0·044 | — |
| 1 | 0·573 | 0·037 | 0·214 | 0·264 | 0·193 | 0·0831 |
| 2 | 0·147 | 0·325 | 0·024 | 0·044 | 0·112 | 0·0961 |
| 3 | — | 0·123 | 0·091 | 0·037 | — | 0·0297 |
| 4 | — | — | 0·083 | 0·031 | 0·023 | — |

Table 3. Results for $v''$-progressions

| $v'$ | $v''$ | Calculated (1) | Calculated (2) | Observed | Calculated (1) / Observed | Calculated (2) / Observed |
|---|---|---|---|---|---|---|
| 0 | 0 | 1·000 | 1·000 | 1·000 | 1·00 | 1·00 |
| | 1 | 0·789 | 0·669 | 0·750 | 1·05 | 0·89 |
| | 2 | 0·249 | 0·282 | 0·365 | 0·68 | 0·77 |
| | 3 | 0·038 | 0·093 | 0·166 | 0·23 | 0·57 |
| | 4 | 0·003 | 0·027 | 0·044 | 0·07 | 0·61 |
| 1 | 0 | 0·669 | 0·789 | 0·573 | 1·16 | 1·38 |
| | 1 | 0·073 | 0·073 | 0·037 | 1·98 | 1·98 |
| | 2 | 0·711 | 0·463 | 0·214 | 3·32 | 2·16 |
| | 3 | 0·491 | 0·416 | 0·264 | 1·86 | 1·57 |
| | 4 | 0·122 | 0·216 | 0·193 | 0·63 | 1·11 |
| 2 | 0 | 0·282 | 0·249 | 0·147 | 1·93 | 1·70 |
| | 1 | 0·463 | 0·711 | 0·325 | 1·42 | 2·18 |
| | 2 | 0·036 | 0·036 | 0·024 | 1·50 | 1·50 |
| | 3 | 0·409 | 0·166 | 0·044 | 9·29 | 3·77 |
| | 4 | 0·621 | 0·369 | 0·112 | 5·54 | 3·25 |
| 3 | 0 | 0·093 | 0·038 | — | — | — |
| | 1 | 0·416 | 0·491 | 0·123 | 3·38 | 3·99 |
| | 2 | 0·166 | 0·409 | 0·091 | 1·82 | 4·48 |
| | 3 | 0·194 | 0·194 | 0·037 | 5·24 | 5·24 |
| | 4 | 0·146 | 0·016 | — | — | — |
| 4 | 0 | 0·027 | 0·003 | — | — | — |
| | 1 | 0·216 | 0·122 | — | — | — |
| | 2 | 0·369 | 0·621 | 0·083 | 4·44 | 7·47 |
| | 3 | 0·016 | 0·146 | 0·031 | 0·51 | 4·69 |
| | 4 | 0·290 | 0·290 | 0·023 | 12·60 | 12·60 |

For actual comparison of the calculated transition probabilities in emission (we will call these the emission probabilities) with the observed $I/\nu^4$ values, we have treated each $v''$-progression independently, and appropriate values are entered in table 3. The second column of this table gives the values of the emission probabilities calculated and entered strictly as suggested by Hutchisson. The fourth column gives the observed $I/\nu^4$ values, while in the fifth column are entered the ratios of these values (calculated to observed $I/\nu^4$). If Hutchisson's theory is correct, these ratios for each separate $v''$-progression should be constant; but, as can easily be noted from the fifth column, the agreement is far from satisfactory.

Besides this, emission probabilities calculated by Hutchisson's method are entered in the third column, after interchanging the quantum numbers: e.g. the value calculated for the (0, 3) band is entered in place of the (3, 0) band and vice versa. The sixth column gives the ratios of these values (Calculated (2)) to the observed $I/\nu^4$. As is evident from a comparison of the values given in the fifth and sixth columns, there is considerable improvement in agreement between the calculated and the observed values, consequent on this interchange of quantum numbers.

## § 5. DISCUSSION OF THE RESULTS

In spite of the improvement just noted, there is not much evidence of a close agreement in general between the observed and the calculated relative intensities for the $N_2$ Second Positive system. With our integrated intensity values for all the measurable bands of the system, the observed values do not fall within the limits required by theory. It is concluded that Hutchisson's theory does not accurately predict intensities in this case. This confirms Langstroth's conclusions from observations of some of the bands of this system on the basis of his peak-intensity measurements.

It is difficult to point out the precise cause of the apparent failure of the theoretical treatment outlined in this work. The theory as applied to this work is based on many assumptions, the chief being the neglect of anharmonicity. The anharmonicity effect sets in with higher vibrational levels, and consequently disagreement should normally increase in the case of bands with higher values of $v'$ and $v''$. This effect must be particularly noticeable in the system under discussion, where a comparatively large number of bands are associated with high $v''$-values. Consequently, not only later bands in each $v''$-progression, but later progressions themselves, will show progressive departure from theoretical values. That this is so can be verified by reference to appropriate columns in table 3.

If one could carry out more complicated and involved calculations according to Hutchisson's modified theory (1931), which takes account of the anharmonicity, it should be possible to test the agreement further. Since the formula suggested is a very complicated expression involving the use of some 91 terms, this problem has been left over for an independent investigation.

Again, there is the probability of external perturbations causing a redistribution of transition probabilities. According to Zener (1933), if appropriate electric fields or collisions induce transitions between attractive and repulsive

states, the probability of these transitions will be a function of perturbations and of the discharge conditions. In these circumstances, the relative intensities in $v''$-progressions are likely to be different from those expected under conditions of an ideal theory. Such a possibility cannot be ruled out altogether in view of Tawde's (1934) experimental results on the $N_2$ Second Positive bands under various complicated conditions. On the other hand, Elliott's (1933) experimental conclusions on the various excitation conditions, obtained for the $N_2$ First Positive system, are altogether contrary to Tawde's. However, this apparent conflict can be resolved if, as suggested by Langstroth (1934, 35), Zener's perturbation effect is a characteristic of particular band systems.

It is also worth while to consider the reasons for the improvement in agreement between observed and calculated values which results on interchange of quantum numbers for the expressions in table 1 of Hutchisson's paper (1930). The effect does not appear to be accidental, for it was also observed by Hutchisson, who showed, from the available experimental data, that his theory in general proves satisfactory in absorption spectra. In the solitary instance in which he has tested it for emission spectra, viz. the $3\,^1B \rightarrow 2\,^1S$ system of $H_2$, he found that the observed values for (1, 0), (2, 1), (3, 2) bands agree better with the calculated values for (0, 1), (1, 2), (2, 3) bands respectively, and vice versa. The initial level in absorption is, of course, the final one in emission, and vice versa. But Hutchisson has not made it clear whether the expressions given in his table 1 for calculating the transition probabilities hold without change both for absorption and emission spectra. Our impression is that the expressions from that table given for any $(n', n'')$ band are applicable intact in the case of bands in absorption. If, however, the transition probability for any $(n', n'')$ band in emission is desired, the same expression has to be used with interchange of subscripts for the constants $b$ and $c$ and $d$ and $e$. The effect of this interchange of subscripts is the same as deriving the transition probability for (1, 2) band in emission from the expression given in that table for the (2, 1) band. If this procedure is not adopted in applying Hutchisson's treatment to emission process, what is calculated as the intensity for the $(x, y)$ band might really be the intensity for the $(y, x)$ band.

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## Part II. LANGSTROTH'S THEORY

*ABSTRACT.* The Second Positive system of $N_2$ was excited as described in Part I above, and integrated intensity values were determined by photographic spectral photometry for all the measurable bands of the system (24 in number, as against only three previously estimated by Langstroth). Transition probabilities in emission ($P^2_{v'v''}$) and the excitation probabilities ($P^2_{v''v'}$) are calculated from the known molecular constants with the help of Hutchisson's formula, and hence the " complete intensities " ($P^2_{v''v'} \times P^2_{v'v''}$) are calculated as suggested by Langstroth. The observed $I/\nu^4$ values (where $I$ is the integrated intensity and $\nu$ the frequency of the band-head) for different bands of the system are compared with the calculated " complete intensities ". The agreement is not satisfactory, even though integrated intensity values are used for comparison. The same conclusion was arrived at by Langstroth from the examination of the peak values determined for fifteen bands of the same system.

The agreement between the observed and the calculated values is considerably improved if, in the calculation of the complete intensity for the $(x, y)$ band, the emission probability ($P^2_{v'v''}$) calculated for the $(x, y)$ band is used. Some reasons for this apparent failure of the theoretical treatment are put forward and discussed.

## §1. INTRODUCTION

LANGSTROTH (1934, 35), has shown that, under certain conditions of excitation, the distribution among the vibrational levels of the initial state in emission can be taken as proportional to the relative excitation probabilities from the ground state, and that the problem of relative excitation probabilities can be solved in the same manner as that of transition probability in emission (i.e. emission probability), as suggested by Hutchisson (1930). Langstroth has developed a simple excitation theory on these lines, by introducing assumptions analogous to those of the emission treatment. When the populations among the vibrational levels of the initial state are known from the excitation probability, these can be used in conjunction with the emission probabilities to predict complete relative intensities of an entire band-system in emission.

Hutchisson's treatment, extended and improved by Langstroth (1934, 35), has opened up a field not only for new investigations on band-spectral intensities, but also for a revision of the existing data on some of the well known band systems. The Second Positive system ($C\,^3\Pi \rightarrow B\,^3\Pi$) of nitrogen, which contains a large number of bands besides those examined by Langstroth, is particularly suitable for such a revision, in view of Tawde's 1934 results and some of the disputable points therein referred to by Langstroth (1934, 35). The agreement between the results calculated with the help of Langstroth's theory and the experimental results both of Langstroth and of Tawde is not satisfactory. This, however, cannot be taken as a failure of the theoretical treatment, since Tawde's results, and most of Langstroth's, were peak-intensity values. It is therefore necessary to examine this theory in the light of more accurate and reliable results, such as integrated intensity values, as recommended by Langstroth.

## §2. THEORETICAL

Langstroth has suggested that, in the excitation of a band-system by direct electron impacts, the relative excitation-probabilities from the various vibrational levels of the ground state can be calculated by Hutchisson's formula. Further, if the supposition is made that all the molecules before excitation exist in the ground state with known vibrational levels, and also that the contribution due to combinations and cascade effects to the populations of the levels of the initial state is negligible, the latter can be taken as proportional to the relative excitation probabilities. From a knowledge of the populations of the initial levels, and of the relative transition probabilities from the initial to the final state, complete relative intensities of the bands of a system may then be predicted. Langstroth has thus deduced the following expression for the complete intensity of a band in an emission system:

$$I_{v'v''} = C_1 P^2_{v'v''} \times P^2_{vv'} \times \nu^4, \qquad \ldots\ldots(2)$$

where $P^2_{vv'}$ is the probability of transition in excitation from the ground state ($v$) to the initial state ($v'$), $P^2_{v'v''}$ is the probability of transition in emission from the initial state ($v'$) to the final state ($v''$), $\nu$ is the frequency of the band-head, and $C_1$ is a constant which is common to all the bands belonging to one system.

In deriving this expression Langstroth made three assumptions: (i) the complete excitation function, like the wave function for a molecule, may be

written as the product of two functions, depending respectively on the electronic and nuclear co-ordinates; (ii) exciting electrons have no direct effect on the nuclei, which are very massive in comparison; and (iii) in excitation the electronic rearrangement of the molecules takes place so rapidly that the nuclear co-ordinates may be considered as unchanged. These assumptions predict a constancy of band-intensity ratios within a system with change in the exciting voltage. If the assumptions are not valid, constancy of ratios will not occur. An experimental test on this point then provides an excellent means of ascertaining whether or not the final equation given above may be expected to give correct results; if so, a comparison between experiment and the intensities calculated from the equation given above furnishes a complete test of the entire theory.

Experimental work reported in Langstroth's first paper (1934) is mostly devoted to clearing up this point about the constancy of band-intensity ratios with varying excitation voltage. The bands 0→2, 1→3, and 2→4 of the $N_2$ Second Positive system were excited by electrons with accelerating potentials between 14 and 160 v. The ratios of the intensities of these bands were found constant with accelerating potentials of more than 30 v., but the ratios were found to vary with voltage below this.

The same point was tested later for three bands of the Negative system of $N_2^+$ and five bands of the Second Positive system of $N_2$ by Hermann (1936), who showed that relative intensities of the bands of a system are entirely independent of the velocity of the exciting electrons.

This being so, the only criterion for the truth of Langstroth's theory is from the accurate data obtained by the integration methods. This test has been made here, and the work covers all the measurable bands of the system, including the fifteen previously reported by Langstroth. Langstroth's conclusions suffer from the fact that, of these fifteen bands, only three were subjected to the rigorous methods of integration. For others, only peak-intensity values were used, as they were assumed to be generally proportional to the values by integration; this assumption, made by Langstroth on the basis of the proportionality between the peak and the integrated values of the 0→2, 1→3, and 2→4 bands of the system, is not, however, entirely justified, as was shown by the present authors (Tawde and Patankar, 1940).

## § 3. RESULTS

The total integrated intensities of all the measurable bands of the $N_2$ Second Positive system were determined with the technique described in Part I above. After applying all the necessary corrections, these intensity values were expressed on a relative scale with (0, 0) band as 1000, and were divided by the appropriate values of $\nu^4$, the values of the frequencies $\nu$ of the band-heads being obtained from the band-head equation of the system, as given in Jevons' *Report* (1932). These observed values of $I/\nu^4$, finally expressed on a relative scale with the value for the (0, 0) band as 1000, are entered in brackets in table 4.

According to Langstroth, the relative values of $I/\nu^4$ can be taken as proportional to the product of $P^2_{v'v''}$ and $P^2_{v v'}$ (equation (2)); our calculated values of the emission probability $P^2_{v'v''}$ are given in table 1 of Part I.

For calculating the excitation probabilities ($P^2_{vv'}$), it is in turn essential to know the values of the internuclear distance $r_0$ and the vibration frequency $\nu_0$ for the ground state ($x^1\Sigma$) and the $c^3\Pi$ state of $N_2$. As any revised data that are available for these quantities do not appreciably differ from those used by Langstroth, we have used his values of the constants $\alpha$ and $\delta$, namely $+0{\cdot}928$

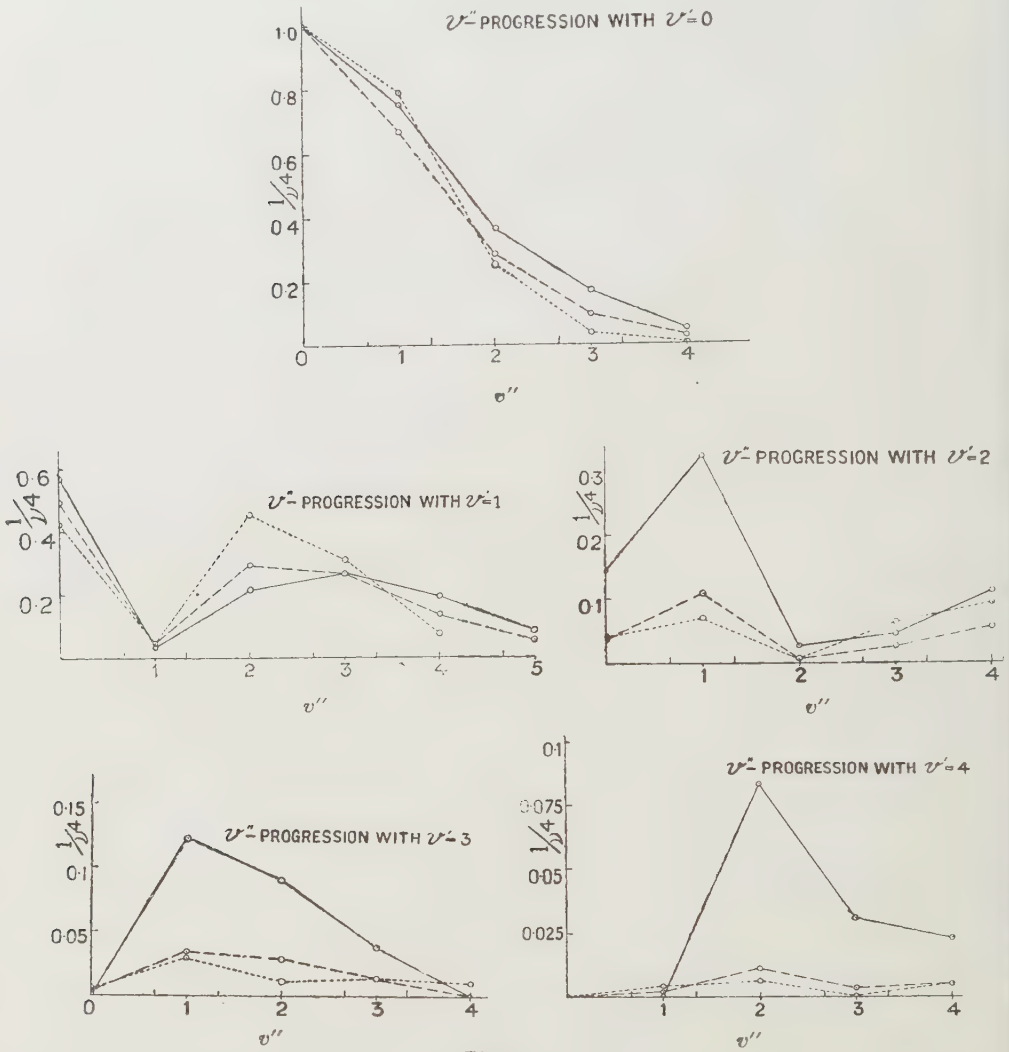


**Figure 1.**

———— observed ; - - - - - - calculated ; — — — — calculated with interchange of quantum numbers $v'$, $v$ .

and $-1{\cdot}096$, respectively; with these we have carried out the calculations for the transition probabilities in excitation. The values of the excitation probabilities thus obtained are as follows:

| Transition ($v^0 \to v'$): | $0\to0$ | $0\to1$ | $0\to2$ | $0\to3$ | $0\to4$ |
|---|---|---|---|---|---|
| Excitation probability ($P^2_{v^0v'}$): | 1·00 | 0·63 | 0·15 | 0·07 | 0·02 |

Supposing that all the molecules, before excitation, exist in the zero level of the ground state, each of these transition probabilities is taken as representing, on a relative scale, the population of the $v'$ level involved in the emission. Next, each value of the emission probability ($P^2_{v'v''}$) in a $v''$-progression from table 1 is multiplied by the appropriate value of $P^2_{v_0v'}$ to give the final calculated value of $I/\nu^4$. These values, which, after Langstroth, we will call the *complete*

Table 4. Calculated complete intensities, and (in brackets) the observed $I/\nu^4$ values

| $v'$ \ $v''$ | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| 0 | 1·000<br>(1·000) | 0·789<br>(0·750) | 0·249<br>(0·365) | 0·038<br>(0·166) | 0·003<br>(0·044) |
| 1 | 0·421<br>(0·573) | 0·046<br>(0·037) | 0·448<br>(0·214) | 0·309<br>(0·264) | 0·077<br>(0·193) |
| 2 | 0·042<br>(0·147) | 0·070<br>(0·325) | 0·005<br>(0·024) | 0·061<br>(0·044) | 0·093<br>(0·112) |
| 3 | 0·006<br>( — ) | 0·028<br>(0·123) | 0·011<br>(0·091) | 0·013<br>(0·037) | 0·010<br>— |
| 4 | 0·0004<br>( — ) | 0·004<br>( — ) | 0·006<br>(0·083) | 0·0003<br>(0·031) | 0·005<br>(0·023) |

Table 5. Calculated complete intensities for emission probabilities after interchange of quantum numbers, and (in brackets) observed $I/\nu^4$ values

| $v'$ \ $v''$ | 0 | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| 0 | 1·000<br>(1·000) | 0·669<br>(0·750) | 0·282<br>(0·365) | 0·093<br>(0·166) | 0·027<br>(0·044) | 0·007<br>( — ) |
| 1 | 0·497<br>(0·573) | 0·046<br>(0·037) | 0·292<br>(0·214) | 0·262<br>(0·264) | 0·136<br>(0·193) | 0·053<br>(0·083) |
| 2 | 0·037<br>(0·147) | 0·107<br>(0·325) | 0·005<br>(0·024) | 0·025<br>(0·044) | 0·055<br>(0·112) | —<br>(0·096) |
| 3 | 0·003<br>( — ) | 0·033<br>(0·123) | 0·027<br>(0·091) | 0·013<br>(0·037) | 0·001<br>( — ) | —<br>(0·030) |
| 4 | 0·00004<br>( — ) | 0·002<br>( — ) | 0·011<br>(0·083) | 0·003<br>(0·031) | 0·005<br>(0·023) | —<br>( — ) |

*intensities*, are entered in table 4; and, for comparison, the observed values of $I/\nu^4$ are entered in brackets below the calculated values.

The values of emission probabilities obtained after interchanging the quantum numbers, as explained in Part I, are also used for getting the complete intensities; the values thus obtained are entered along with the observed values of $I/\nu^4$ in table 5. The comparison between the observed values and both

sets of calculated complete intensities is shown graphically in figure 1 for each separate $v''$-progression.

## §4. DISCUSSION OF THE RESULTS

It will be seen from tables 4 and 5 and the graphs that the calculated values along the $v''$-progressions with $v'=2$, 3, and 4 are too low compared with the observed values; in neither table is the agreement satisfactory. The complete intensity values calculated with the emission probabilities obtained after interchange of quantum numbers, however, show a better general agreement with the observed values.

Generally there is less departure in bands associated with low vibrational quantum numbers. This may be attributed to the fact that Hutchisson's (1930) theory, according to which these calculations are made, takes no account of the anharmonicity effect, which must be more important for bands with higher quantum nunbers. An improved theory, which includes the anharmonicity effect, has been given by Hutchisson in his second paper (1931); the formula suggested involves about 91 terms, calculations of which are too complicated for inclusion in the present work, but may serve as a subject for an independent investigation. Again, there is the possibility that the disagreement may be due to the presence of external perturbations causing a redistribution of transition probabilities. Both these effects have been fully discussed in Part I.

Further, the excitation probability factor may not correctly take into account the true state of electronic transitions. Langstroth's excitation probabilities are calculated on the assumption that the populations of the initial levels are predominantly due to excitation by electron impacts direct from the zero vibrational level of the ground state. It may be that, before excitation, a considerable number of molecules are distributed in levels of the ground state higher than the zero vibrational level. If this is the case, transitions due to excitation from these levels, as well as from the zero level, might also contribute to the populations in the initial state of the emission system. There is also a possibility of some contribution to these populations due to combinations and cascade effects. If such a state of affairs exists in the electrical excitation causing the emission of bands of the $N_2$ Second Positive system, the distribution factor for levels of the initial state would be different from the one calculated under the assumptions of Langstroth's excitation theory, and each of the progressions would show an entirely different scale of complete intensities, perhaps more in agreement with the observed results. In order to test this point we shall have to await further improvements in the excitation theory.

As regards the invalidity of the assumptions introduced in Langstroth's excitation treatment for a certain range of the excitation voltage, the evidence is conflicting. The criterion for the applicability of Langstroth's expression is the constancy of band-intensity ratios with varying exciting voltages. While Langstroth's own observations indicate the constancy only above the exciting energy of 30 e.v., Hermann's (1936) results do not show any such dependence; in the absence of further material critical discussion of this point is not possible, but Langstroth's treatment is undoubtedly applicable to our problem, as the exciting energy in our discharge tube was above 30 ev.; this is supported

by the fact that Langstroth himself examines his theory with reference to Tawde's (1934) results on $N_2$ under widely differing excitation conditions, such as Giessler discharge, spark, electrodeless discharge, etc.

The improvement in agreement between the calculated and the observed values on interchange of quantum numbers has also been fully discussed in Part I. This correction is necessary in calculating the emission probability ($P^2_{v'v''}$), but not in evaluating the excitation probability ($P^2_{v''v'}$), since in this case the transitions are similar to those in excitation.

The results presented here are believed to be far more extensive and accurate than any so far obtained on the type of problem under investigation. Any discrepancies between the results and the theory must be attributed either to incompleteness in the theory or to some interference with the assumed mechanism of excitation, or to both causes.

## § 5. ACKNOWLEDGEMENTS

The authors express their sincere thanks to Prof. G. R. Paranjpe, Principal of the Royal Institute of Science, Bombay, for placing at their disposal all the necessary facilities, and to Sir C. V. Raman, F.R.S., for kindly allowing them the use of the self-recording microphotometer at the Indian Institute of Science, Bangalore.

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# DISCUSSION

## On paper by Dr. D. S. Evans and Dr. K. Mendelssohn ("The physics of blood-pressure measurement", *Proc. Phys. Soc.* **54**, 211–219, 1942).

Professor R. R. Macintosh and Dr. S. L. Cowan. This paper has come to our notice only recently,* and since the authors express their "thanks to Professor R. R. Macintosh, of the Department of Anaesthetics, Oxford University, who formulated the medical problem, and to the staff of the Department for their interest and help in the clinical experiments", we feel that it should be made clear that these clinical experiments are not the ones to which Evans and Mendelssohn refer as confirming the results derived from their theory (§ 5 and Abstract). Our collaboration with Evans and Mendelssohn ceased in January 1942. These confirmatory clinical tests must have been carried out later, with the co-operation of other physiologists or medical men than ourselves. No copy or draft of the paper was shown before publication to any member of the Department.

Dr. S. L. Cowan. Apart from the points raised in the above contribution, the scientific members of the Department feel that since no details of these tests are included in the paper and, in particular, since there are no results of laboratory experiments, e.g. comparing the readings of the new instruments with those obtained by direct cannulation of arteries, we are unable to form an opinion on how far the results obtained support their theoretical treatment and its implications (p. 216, line 4 ; § 4, line 10 ; p. 214, line 6 from bottom). We feel that the authors have not made sufficiently clear the basis of their claims for the instrument.

To save space, we propose to raise only the more important questions.

1. Although Evans and Mendelssohn claim novel results, we do not see in what points the apparatus differs significantly from those which other authors have described for the indirect measurement of blood pressure. The use of a differential manometer with capillary leak and the oscillometric method was described by Erlanger (1904) and by Pachon (1909). Since then many similar forms of apparatus have been described, e.g. Savitzky (1936), Menard (1937), and some of them manufactured in numbers (Plesch, 1930).

2. Of the "fundamentally different" (footnote, p. 212) methods employed by Evans and Mendelssohn for determining diastolic, systolic and pulse pressures, the first seems to us the same as that originally used by Pachon, the second to have been used by Kolls (1920) and Darrow (1937, figure 1 B, and p. 386, lines 21 ff.), and the third seems to have no experimental foundation, since the inferences drawn by Sahli from his experiments have been shown to be wrong (e.g. Straub and Kroetz, 1925, in particular pp. 224–5, Table I for cuff pressures 20 to 60 mm. Hg; Broemser and Liedholm, 1936, pp. 314–15).

3. The use of Hooke's law in equation (4) seems unjustified, since experimental observations with arteries show that the volume elasticity modulus usually increases when the resultant pressure on the arterial wall (difference between blood pressure and cuff pressure) rises from zero to pressures between systolic and diastolic (Bramwell, McDowall and McSwiney, 1923 ; Frank and Wetzler, 1931). Similar changes of volume elasticity are observed in finite deformations of elastic tubes (Frank, 1928).

4. The authors treat the transmission of arterial volume pulsations to the manometer as a purely static process, except in estimating the distortion due to the capillary shunt across the manometer (§ 4, lines 12 ff.). This ignores the work of other observers on important causes of distortion : e.g. the reaction of the transmitting system on the manometer proper (Frank, 1929) ; the pressure waves set up in the system (Brewer *et al.*, 1934) ; and the distorting and integrating effect of the cuff (Ranke, 1935), which by itself seems to invalidate the authors' claim to obtain accurate records of the pulse curve.

* The paper was published on 1 May 1942, the MS. having been received on 17 December 1941. The first intimation that Professor Macintosh and Dr. Cowan wished to contribute to a discussion was received 16 November 1942.—Ed.

5. At one place (p. 215), in connection with the systolic region (figure 2, II and III), the authors refer to a dynamical effect (lines 7 ff.) of blood flow which limits the validity of the quantitative relationship. But why is it that similar dynamical effects should not transform the sudden jump in amplitude of volume pulsations at the diastolic pressure (transition from regions I to II, figure 2) into a more gradual rise, as has been found with other arterial oscillographs ?

6. Considering questions 3 and 5 together, it appears that the authors' method for determining the *pulse* pressure can neither give true values nor distinguish between a rise in pulse pressure, on the one hand, and, on the other, a decrease of diastolic pressure at constant pulse pressure.

7. The authors' remarks about the reason for the causes of Korotkov sounds being unknown do little justice to the extensive work which has been done on the subject (e.g., Bramwell and Hickson, 1926 ; Frank and Wetzler, 1931). It has been shown that owing to the change in the contour of the pressure pulse passing underneath an inflated cuff, strong high-frequency components are produced at certain cuff-pressures, which can give rise to audible vibrations (Brewer *et al.*, 1934, p. 424, lines 19 ff.).

Dr. H. Heller. The determination of the blood pressure is not " the only means for the early detection of shock ", and, in fact, shock without low blood pressure has been recorded.

There is no basis for the statement that the " various modes of operation hitherto employed are *fundamentally* different from ours ". Acquaintance with the history of the technique of indirect blood-pressure measurement should make that clear (see, for example, Pachon (1909), Erlanger (1916 and 1921), Plesch (1930), McLeod (1943) and Wiggers (1937, p. 613).

With reference to p. 216, when the authors say, " Reference to equation (6) shows that when the external pressure is less than $p_d$ the amplitude of oscillation in B is proportional to $p_0$", it must be remembered that this conclusion is only true in so far as equation (6) itself is true, and the deduction is rather that the amplitude *would be expected to be* proportional to $p_0$.

Any other criticisms which I would have made are in the contribution by Professor Macintosh and Dr. Cowan, which they have kindly allowed me to see, but, generally speaking, it seems to me that no experimental results were offered as proofs for the contentions in § 5 (Conclusion). The desirability of control experiments on animals (comparison with direct blood-pressure measurements) is not mentioned.

Dr. J. Plesch. The article consists of two parts : first, a theoretical analysis of the conditions inside the inflated cuff of a blood-pressure recording apparatus and in the manometer registering this pressure, and second, the description of independent methods for the determination of the systolic, diastolic and pulse pressures.

The theoretical analysis rests, in my opinion, on an untenable assumption, expressed in equation (4).

This equation means that the unstressed artery has no definite volume ; in other words, that if the pressure inside the artery is the same as outside, the artery may be completely collapsed or completely round. According to my experience a considerable outside pressure is needed to make the artery collapse : in the case of healthy adults some 20 to 30 mm. Hg, and in the case of certain sclerotic patients as much as 50 mm. Hg or more. If the outside pressure exceeds the internal by less than this amount, the cross-section of the artery becomes first oval, then dumb-bell-shaped, and there is a definite uni-valued relation between outside pressure and cross-section.

Equation (4) further implies that the tissues of the arm are incompressible and free from friction. If one compares blood-pressure diagrams obtained from patients with slender arms with others from patients with less slender arms, one cannot fail to see that this assumption must be wrong.

Finally, it takes no notice of the influence of the accelerations and the mass of the moving parts and of the elasticity of the tissues, air and rubber, all of which play an important part in determining the actual size of the oscillations.

In view of all this, I am convinced that the criteria given for the determination of the diastolic and pulse pressures on the strength of equation (4) are false.

With regard to the determination of the systolic pressure, which, though independent of this theoretical analysis, still rests on the assumption that blood starts to flow when the pressure in the upper cuff falls below the systolic, I have the same objection, namely, that actually blood begins to flow before the pressure in the upper cuff falls below systolic as soon as that pressure exceeds systolic by less than the critical pressure discussed above.

This leads us to the consideration of the second part of the article—the arrangement of the recording system.

As far as the one-cuff arrangement and the determination of the diastolic pressure is concerned, there is not much new in the arrangement. Optical registration is probably better than graphic registration or none at all; but whether the inherent complication does not destroy its clinical value is a rather moot point. As far as the systolic pressure is concerned, it should be borne in mind that pulsations, phenomena registered by the capillary-bypassed manometer, are not identical with blood flow, and that, therefore, we have no right to assume that the lower cuff will yield visible oscillation as soon as the blood flow starts. It is therefore safer to use one single cuff for the determination of the systolic pressure and to rely on well established criteria for its determination.

Dr. F. Barnett Mallinson. The criticism of the paper by Evans and Mendelssohn is mainly levelled at the performance of an instrument and the clinical results obtained with it, neither of which is described in the paper. It may be of value, therefore, to record some practical experiences of the method from the anaesthetist's point of view.

I have had the opportunity of using this instrument over a considerable period of time at a large E.M.S. hospital upon upwards of 100 operation cases in which shock of varying degrees of severity developed. These included a number of men severely traumatized and shocked as the result of injuries sustained in the course of military duties.

I have been particularly interested for a number of years in attaining an improved method of visual blood-pressure recording, because of the possibility which it presents of overcoming the serious disadvantages associated with auditory methods. From my practical experience I can endorse to the full the remarks of Evans and Mendelssohn on the difficulties of the auditory method in the operating theatre (page 212 of their paper). I have found that the method described by Evans and Mendelssohn possesses the following signal advantages over other machines employing visual recording :—

(1) Systolic pressure is much more sharply defined, " edge effects " being reduced to a minimum.

(2) The striking sharpness of the discontinuity in the ($\Delta P$, $P$) curve gives a far closer and more readily interpreted definition of diastolic pressure than hitherto.

(3) The continuous recording of pulse pressure is a feature quite new to me in blood-pressure recording, which is of especial value in " touch-and-go " periods, when the anaesthetist is fully occupied with blood transfusion and other resuscitation measures, and cannot spare time to take systolic and diastolic readings.

I cannot, therefore, concur in the " theoretical " criticisms advanced by Macintosh, Cowan and Plesch, since they are not in any way borne out by practical observation with the instrument. The practical medical man, fully aware of the complexity of his subject, knows only too well the awful chasm which so often separates medical theory and practice. It is therefore by its practical performance that the method of Evans and Mendelssohn must be judged.

The method is, in my opinion, a most timely contribution, on which the authors are to be congratulated. This is well supported by the very favourable reception accorded to their work by my colleagues when it was presented at a recent meeting of the Section of Anaesthetics of the Royal Society of Medicine.

Authors' reply. We much regret that the character of Professor Macintosh's remarks concerning our collaboration with his Department, and of some of the scientific arguments used by his staff, oblige us to reply with a candour which we should like to have avoided. We had certainly no reason to submit a manuscript to Professor Macintosh for approval, since it had been made quite clear to him in writing (letter dated 6.10.41) that our paper would be published from the Clarendon Laboratory, and not from his Department. This decision, to which he himself had agreed, had been taken because the whole work

lay, in our opinion, outside the domain of his Department, and had, in fact, except for the clinical tests, been carried out exclusively at the Clarendon Laboratory.

What Professor Macintosh does not mention is, that not only was he himself, together with members of his Department, fully acquainted with the contents of our paper *before* publication, but that, in addition, their criticism was explicitly invited at that time. *No such criticism was, however, made by any of them.* On the contrary, until collaboration between Professor Macintosh and ourselves ceased—for reasons quite unconnected with the work now under discussion—he expressed appreciation of the value of our work on numerous occasions—verbally, in writing and by implication. For example, the annual report for 1940–41 of the Nuffield Department of Anaesthetics, of which Professor Macintosh is the head, contains the words :—" Work has been carried out by Dr. K. Mendelssohn and Dr. D. S. Evans to construct a machine to record blood pressure continuously. The present apparatus records the systolic and diastolic pressures visually ".* It appears that he *now* doubts these features of our method.

The clinical experiments referred to in § 5 of our paper were carried out at the Radcliffe Infirmary, Oxford, between 1 May and 1 November 1941, i.e. *before* collaboration ceased. They consisted of tests of the working model of our apparatus at about 100 surgical operations. At all these cases we enjoyed the help and interest of at least one member of the Nuffield Department of Anaesthetics, who attended them in their capacity as anaesthetists, and we consider it only fair that we should have expressed our thanks to them. Since the name of the anaesthetist attending each case was not kept in our records, and since all six anaesthetists mainly concerned have left Professor Macintosh's Department, we regret that we are unable to apportion our thanks in individual shares. We cannot assume that Professor Macintosh was ignorant of the conditions then obtaining, since, in a letter by one of us (K. M.), addressed to him on 13 January 1942, the receipt of which was acknowledged by him on the same day, there occurs the following sentence :— " As recently as October 1941 you expressed your approval of our work, which had then passed the clinical tests, and had been demonstrated to representatives of the Services ". In the circumstances we cannot but consider Professor Macintosh's remarks as most unfortunate. All arrangements concerning collaboration were made solely between ourselves and Professor Macintosh in his capacity as head of the Department, since we assumed that he alone was concerned with such administrative questions.

Dr. Cowan's contention that (unnamed) " scientific members of the Department " feel the need to criticize our paper requires some comment. It appears that their criticism of our work is based, not on any observations of their own which are contrary to our results (as far as we know no research on blood-pressure determination has ever been carried out at the Nuffield Department of Anaesthetics), but rests solely on references selected from an extensive, and in places controversial, literature. We consider it therefore significant that of the four well-known physiologists, all experts in the field, who, we understand, at the suggestion of our critics, were originally invited to this discussion, *not one* has cared to support their statements.

Dr. Cowan's comment on the lack of comparison of our results with those obtained by direct cannulation of the artery may give the impression that such a check is customary in work on the indirect determination of blood pressure. It evidently has escaped his notice that *not one* of the seven authors of papers on blood-pressure indicators quoted by him (Erlanger (1904), Pachon, Savitzky, Menard, Kolls, Darrow and Plesch) employs this check. Indeed, such a check is unnecessary, since Hamilton, Woodbury and Harper (1936) have demonstrated that there exists no significant difference between the values obtained by direct cannulation and those obtained by the indirect method.

Dr. Cowan's contribution ends with a number of detailed points which may conveniently be dealt with *seriatim*.

Points 1 and 2 :—

Dr. Cowan's reference to the " fundamentally different " methods employed by us is incorrect, for examination of our paper will show that the only time the words " fundamentally different " are used (footnote, p. 212) they refer clearly to the particular use of a double cuff only.

* *Oxford University Gazette*, Supplement to No. 2363.

We are satisfied that a careful reading of our paper as far as the second sentence will make it clear that we did *not* claim any originality for our method or apparatus, but, on the contrary, stated explicitly that we were concerned with " the development of existing methods ". It appears, however, from the papers quoted by Dr. Cowan, that our statement erred on the side of modesty, and that our method or, rather, combination of methods, is quite original. We trust that the following table will help to emphasize the significant differences between these devices and our own.

Essential features

| Author | Double cuff | Differential manometer | Capillary | Light beam and scale |
|---|---|---|---|---|
| Evans and Mendelssohn | + | + | + | + |
| Pachon | — | + | — | — |
| Erlanger | — | — | + | — |
| Savitzky | — | + | ? | + |
| Menard | + | + | — | — |
| Plesch | — | + | + | — |
| Kolls | + | — | — | — |

The method of Darrow differs so completely that it cannot even be comprehended in this system of classification. We have equally failed to detect any statement in the paper by Straub and Kroetz (1925) which is contradictory to the arguments in our paper. This is not very surprising, since their results (figure 2, p. 239—pressures up to 40 mm.) can be expressed very well by our equation (4). Dr. Cowan's argument appears to derive even less support from the paper by Broemser and Liedholm (1936), which he quotes. On the contrary, these authors are in full agreement with us as regards the applicability of the compression method up to and including diastolic pressure (paragraph 1 of their summary, p. 328).

Point 3 :—

It is generally recognized that in order to make physiological phenomena amenable to mathematical treatment, some simplification is necessary. The test of the legitimacy of such simplifications (in our case the application of Hooke's law to the artery) is the comparison of the theoretical predictions with experimental results.

We thought we had made it quite clear that this simplification was justified in our statement that the clinical results "have borne out the features of the theoretical ($\Delta P$, $P$) curve " (§ 5 of our paper). The excellent agreement between the theoretical and experimental ($\Delta P$, $P$) curves (Evans and Mendelssohn, 1943) will make this clear. While our results differ from an early *indirect* determination of arterial elasticity by Bramwell and others (which Dr. Cowan quotes), they are in agreement with the more recent *direct* determinations by Hallock and Benson (1937). The indirect method has since been the subject of criticism by Wiggers (1939, p. 540).

Dr. Cowan's argument also overlooks the fact, stressed by all text-books of physiology, that arterial elasticity is variable, and changes for one and the same vessel with the degree of relaxation. Wiggers (1937) shows that while in a relaxed artery the deviations from Hooke's law are negative (p. 528, figure 104, curve A), they are of opposite sign when the artery is strongly contracted (curve C), while for moderate contraction (curve B) the relation is, to a first approximation, linear. Hence our use of Hooke's law as a first approximation.

The other two papers which Dr. Cowan quotes (Frank, 1928 ; Frank and Wetzler, 1931) seem to bear little relation to the argument.

Point 4 :—

Extensive calculations of the effects of the transmission system, and of many other causes of perturbation not mentioned by Dr. Cowan, were made, and are clearly referred

to on p. 218 of our paper. However, since it is not usual to include in papers in physics periodicals long-winded accounts of calculations which do not influence the stated results, the details were omitted. For example, the integrating effect on the short period components of the pulse curve, mentioned by Dr. Cowan, is negligible in any practical case because the numerical values of the coefficients of these Fourier components are very small. In fact, pulse wave recording from an inflated cuff is a standard practice in circulatory studies. Numerous references to this " oscillometric " method can be found in any text-book of physiology. A detailed discussion on the negligibility of these effects was given by one of us (D. S. E.) to the Nuffield Department of Anaesthetics late in 1941.

Point 5 :—

It should be clear from our paper that the effect referred to by Dr. Cowan is not, as he assumes, a dynamical, but a simple volume effect. It therefore does not influence the width of the transition at diastolic pressure, which is determined by $(\Delta P/P)$ and by the natural variation of the blood pressure with respiration.

Point 6 :—

The principles of logic make it unnecessary to refute this point separately, since points 3 and 5, on which it depends, have already been dealt with.

Point 7 :—

This point does not seem to require an answer, since it is based on an incorrect reference to our paper. If Dr. Cowan will examine line 12, p. 212, of our paper, he will notice that we stated that the reason for the " *change in* " and not, as he assumes, the " *causes of* ", the Korotkov sounds was unknown.

We cannot in any case share Dr. Cowan's optimism that the existence of the pulse sounds is adequately explained by the occurrence of " strong high-frequency components " (whatever they may be). Not being physiologists, we do not wish to offer an opinion as to which of the many attempts at explanation may ultimately prove to be correct. We can do no more than quote Wiggers (1939, p. 644) : " As to the cause of turbulence, opinions are divided ".

In reply to Dr. Heller, we fail to detect the relevance of his remarks on the subject of shock to the topic of discussion. However, since the Government publication on shock * provides a ready answer, this may be quoted : " Indications that shock is developing or progressing are : a rising pulse rate, a decrease in pulse pressure (difference between systolic and diastolic values), increasing pallor, and the onset of sweating ". The last two signs may be difficult to observe in the draped and anaesthetized patient on the operating table. The assessment of the remaining two signs is precisely the object of our method.

Dr. Heller then takes exception to our footnote on p. 212, which states that the mode of operation of our double cuff differs fundamentally from those employed hitherto. He remarks that " acquaintance with the history of the technique of indirect blood-pressure measurement " should make it clear that " there is no basis " for this statement. He quotes in support of this somewhat sweeping assertion four papers (Pachon, 1909 ; Erlanger, 1916 and 1921 ; Plesch, 1930), two of which deal with one-cuff methods, and two of which relate to experiments on excised arteries. Consequently none of the papers quoted by him bears even the remotest relation to the present argument. We trust that Dr. Heller himself will find the significant differences when comparing our method with other two-cuff methods (e.g. Menard, 1937), but we consider it deplorable that he should have gone out of his way to indulge in argument of this character.

His last point requires no answer, since the expectation of a mathematical deduction is generally agreed to be unity.

Finally, turning to Dr. Plesch, who, like Dr. Heller, has entered this discussion at the suggestion of Professor Macintosh, we think that his arguments against our equation (4) have already been met in the reply to Dr. Cowan's Point 3. His " experience " that " a considerable outside pressure is needed to make the artery collapse ", together with

* Medical Research Council, War Memorandum No. 1, H.M. Stationery Office, London, 1940.

his statements concerning the rigidity of the tissues, are surprising. Wiggers, in his text-book on physiology (1939), states quite clearly that " the criteria employed presuppose that the arterial walls and surrounding tissues of the arm offer no appreciable resistance to compression. It is generally agreed that this is true, provided the cuff used for adults has a width of 12 cm."

Dr. Plesch's objection concerning the measurement of systolic pressure applies to *all* methods of blood-pressure determination which employ an occluding cuff, and is in any case refuted by direct experiment (Hamilton, Woodbury and Harper, loc. cit.). We do not propose to enter into a discussion of the hypothetical phenomena which Dr. Plesch expects to occur in an artery of " dumb-bell-shaped cross-section ", more especially since the author has thereby landed himself in a contradiction. He states that he is " convinced that the criteria given " by us " for the determination of the diastolic and pulse pressures . . . . are false ". Our criterion for diastolic (p. 214) is the sudden drop of the oscillations. Dr. Plesch, in one of his own papers, states that " *Der diastolische Blutdruck liegt also da, wo die Oszillationen plötzlich abfallen* " (his italics) (the diastolic pressure is marked by the sudden drop of the oscillations) (Plesch, 1930). We fail to see why the same criterion is false when stated by ourselves, but true when stated by Dr. Plesch.

Since neither of us has ever met Dr. Plesch, we assume that his opinion is not based on any practical experience with our method, facilities for the trial of which would gladly have been granted to him.

The theoretical objections to our method advanced in this discussion lag, as is only natural in war-time, some distance behind the practical developments. We think that Dr. Mallinson's contribution shows that our method has, meanwhile, in spite of the theoretical demonstration of its impossibility, given a good account of itself. It has also been employed (in slightly modified forms) in three Government research establishments, and has since been demonstrated before the Royal Society of Medicine. Detailed accounts of the construction of the apparatus, of clinical observations, and of the physiological significance of our mathematical treatment, are being, or will be, published in appropriate journals.

In conclusion we should like to mention that when Professor Macintosh and his friends first submitted their comments, we pointed out that, as was clearly stated in paragraph 5 of our paper, these questions of apparatus, description and the discussion of clinical results would, in any case, be the subject of a publication by ourselves in a medical journal. It was only Professor Macintosh's insistence on raising the matter in its present form which compelled us to take part in what is, to our mind, a somewhat unedifying controversy, and one which we should like to have avoided at a time when our energies might have been put to more constructive use.

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# CURRENT PROBLEMS IN VISUAL FUNCTION AND VISUAL PERCEPTION

By F. C. BARTLETT

*Thirteenth Thomas Young Oration, delivered* 4 *June* 1943

## § 1. INTRODUCTION

I have often wondered what would happen if some great man in whose honour a lecture is periodically delivered could be resurrected for the occasion and, having acquired an adequate knowledge of the present, could pronounce an oration upon his own past achievements. Spurred on, partly, by this engaging, if speculative, consideration, I have lately been studying more carefully than before many of the published works and letters of Thomas Young, and I have read the elegant, though far from exciting, biography published twenty-six years after the great man's death by the Reverend Professor George Peacock. Is it conceivable that this acute, meticulous, rather stubborn and humourless but wide-ranging mind would, under any circumstances, ever attempt to set its achievements in a frame of developing psychological knowledge? At first, I must confess, even my faint hopes were considerably dashed. What possible psychological interests could be entertained by one who as a child never played a game, who was a "unique example of unassisted education", who made "few or no sacrifices to the pleasures of the imagination", who was known to the undergraduates of Emmanuel College, Cambridge, as "Phenomenon Young", and of whom it was recorded, perhaps a little unfairly, that "he took no delight in the pleasures of the table and could never either make a joke or understand one"? It seems a strange fact that a man who throughout his life occupied himself solidly with objective facts and principles, objectively recorded and interpreted, should, mainly on the strength of a few sentences from two papers contributed to the Royal Society before he was thirty years of age, find a place in every psychological text-book, and be hailed as a genuine founder of a most important branch of psychological investigation.

Yet, as I pursued my reading, I found a few cheering counter-indications. When, a medical student at length, Young removed from the austere life of London to the gayer circles of Edinburgh and the Scottish Highlands, signs appeared of an awakening interest in human behaviour. He records how once he fell in with an argumentative party of lairds and dined with them. "I remained occupied in my own defence and in studying the various appearances of human nature until three o'clock in the morning". Here his conscientious biographer

remarks: "It is hardly necessary to add that Young was habitually temperate". There is, however, no evidence that he took advantage of this possible opportunity to study the phenomena of double vision. He danced reels, he sang, he played music, he wrote verses—all very badly, but still he did them. He began to observe people, especially the fairer ones, and the more noble they were, the more notice he gave them. He left the home of the Duke of Argyle with regret, sorry that he had little time to "observe the beauties of Inverary". These, somewhat to the reader's surprise perhaps, he goes on to specify: "Lady Charlotte is handsomer than Lady Augusta, she sings better, but she has less good sense, and less sweetness: an innocent giddiness sometimes gives her the appearance of a little affectation: She is to Lady Augusta what Venus is to Minerva: I suppose she wishes for no more. Both are Goddesses". Perhaps, after all, hidden deep within that formal and somewhat aloof character, was a psychologist of a sort.

I have found one reference to psychology in his publications. There may be others, and if so, the implication is almost certain to be the same. When Young went to Göttingen in the pursuit of his medical studies, among the lectures he attended were some by Professor Spittler on *The History and Constitution of the European States*. He thought them good, though, as customary, there is a hint of defect. "Possessing very great merit, as well in a moral and psychological sense as in an historical view; and though the mere historical facts may escape the memory of his hearers, yet they cannot fail to profit, if they have paid sufficient attention, by the conclusions they are taught to draw".

No doubt Thomas Young could not have been expected to think of psychology as being in any way concerned with "mere historical facts". He was pioneer enough, in all conscience, without being as daring as that. It is, however, not a wholly wild supposition, I think, that if he could return to a world in which it is becoming apparent to all that man cannot control nature without disaster unless he can understand and guide his own behaviour, he might feel pleased rather than pained to find here and there a psychologist to do him honour. One thing at least is absolutely certain. If he had himself pushed further along the path which he at first seemed to be marking out for himself, and if he had continued to investigate the acting mechanism of the eye and, through this, of the other senses too, it would have been with an experimental approach.

I do not wish to deceive myself. Could Thomas Young now deliver the Thomas Young Oration I would risk nothing that I deeply value on the remote chance that he would propound any psychological problems. Still, he might, and if he did it is certain that his approach, like mine, would be by way of the experimental facts. With this rather tepid comfort, I must proceed.

## § 2. VISUAL ACCOMMODATION

It is fitting that I should begin by a reference to some interesting and curious problems of visual accommodation. For this was the subject of Young's first great triumph. When he was still only nineteen years of age he read his paper dealing mainly with the mechanism of accommodation before the Royal Society. He was not the first in the field, and said so, but he was the first to develop a

clear and detailed picture of the mechanism of control of the crystalline lens. His views suffered a temporary eclipse, but the shadow passed, and seven years later he returned to the same topic with his second famous paper, which finally established the manner in which the eye is accommodated to near or more distant vision.

The mechanism was discovered a hundred and fifty years ago. Yet a number of problems are now becoming acute which have to do with the ways in which this and the other musculature of the eye work, and they are still unsolved. The eye is the predominant human sense. It guides the great bulk of man's behaviour. It is controlled by a beautiful and delicate muscle system, variations in which are relatively easily and decisively recorded, and have their definite correlates in action. On general grounds it seems possible, or even probable, that many specific deteriorations in behaviour, whether temporary or permanent, are rapidly, decisively and measurably mirrored by some disturbance in the functional efficiency of the muscles which control accommodation, convergence and other eye movements. Some facts are known and support this suggestion, but many more are needed.

The near-point of retinal accommodation proceeds with exercise and then recedes as fatigue accumulates (McFarland *et al.*, 1942). Accommodation time appears to be the only known measure (other than a purely auditory one) which is immediately and significantly affected by very loud sound (Stevens, 1943). There is evidence that accommodation time increases consistently with age (Banister and Pollock, 1928), and conversely that a low accommodation threshold is correlated positively with efficiency in games and occupations which demand the rapid manipulation of moving objects (Banister and Pollock, 1928). In a recent extremely interesting experiment a number of subjects were pushed near to their physiological limits by a very punishing physical exercise. As soon as they had recovered sufficiently their accommodation times were taken under accurately controlled conditions. They had significantly increased, but in about half an hour were back to normal again (Frankau). There are some puzzling features about this experiment, for when it was repeated a few times the accommodation effect sometimes disappeared. Whether, therefore, it was due to the general confusion set up by the novelty of the exercise, or to the actual physiological effect of metabolites produced by the violent bodily activity, remains at present uncertain. What is certain is that a general and widely spread physical or mental disturbance may be mirrored by a measurable change in the speed of retinal accommodation. Finally, it is now being reported over and over again that certain psycho-neurotic disturbances, especially those that are rather vaguely collected under the name of "fatigue syndrome", have as their most prominent symptoms visual irregularities usually inadequately described as a "blurring of the visual field". A survey of visual acuity thresholds in a group of psycho-neurotics as compared with those in a normal population has revealed a significant rise of threshold in the former (Slater). Again the reported effect needs further analysis. It may be that the fault lies in the accommodation mechanism, or in the control of convergence or other eye movements, or (though this seems less likely) directly in visual acuity itself.

It is not accommodation functions only that demand this kind of study, designed to set them into relation with general facts of behaviour. Long ago Dodge and others (1901, 15) showed that the efficiency of lateral eye movements is affected by physiological and physical conditions not themselves of visual origin. More lately Miles (1919), repeating their procedure, has demonstrated that of all measures these seem to give the best estimate of the effects of prolonged low diet.

In many ways it thus appears that the muscle system of the eye, which Young began to describe so long since, may have intimate connections with a variety of phenomena of general human behaviour. There is nothing surprising in this. What is surprising is that these connections have escaped adequate quantitative investigation. The time is ripe for an organized research into the most reliable and practicable technique for recording every aspect of function of the eye-muscle system. Age norms are needed for all these, and an experimental study of the main conditions of departure from these norms. It is not impossible that this would yield the best diagnostic signs that are available for several directions of human efficiency and inefficiency, especially in this highly mechanized age, when machine control constantly demands a high and maintained level of visual function.

### § 3. COMBINED STUMILI

The second group of problems which I wish to raise are perhaps of more fundamental interest still, because their theoretical basis is even less fully understood. That Young himself might have been extremely attracted to these requires no great stretch of imagination. His championship of the undulatory theory was based, at least partly, on his application of certain of the phenomena of sound to problems of light. Now, in all these years, an immense amount of detailed and valuable knowledge has been amassed about the conditions of reaction of each of the special sense mechanisms. We know much about how the eye, the ear, the skin respond to their appropriate stimuli. But in actual life a special sense rarely behaves by itself, so to speak. Visual, auditory, tactile and other cues of like order are all present and effective together, and combine to take charge of our conduct. I believe that the next really great advances in special sense study will have to be concerned with the conjoint, or integrated, action of different sensory modes.

Let me illustrate this. There is a well known illusion which has been simply described as follows:

"If a person holding his two arms outstretched horizontally before him raises one to an angle about 45° above the horizontal and holds it in this position for about 30 seconds; and if he, then, follows instructions to close his eyes and bring the raised arm to the same position as the other, the horizontal one, in general the arm will not return to the horizontal position, but to a position nearer to the previous raised one" (Hoff and Schilder, 1925).

It is very easily possible to construct an experimental setting in which the upward and downward movements of the outstretched arm cause a spot of light to move over a scale—the actual arm movements being obscured from sight—and the central position on the scale coincides in all cases with the final required

arm-level. Such an arrangement sets up a state of conflict between visual impressions and kinaesthetic and postural impressions, since the latter indicate that the descending arm is in the required position when the former indicate that further adjustment is necessary.

Generally, when visual cues and others conflict, one tends to assume that in man the visual impressions will take the lead. The experiment was performed with three types of instruction. The first, which may be called "neutral", gave no specific information. The subject's attention was called to the scale, but nothing was said about the significance of the location of the spot of light. The second gave a tentative visual bias, the subject being informed that when the spot was central on the scale he would probably find that his arms were level. The third gave a definite visual bias: it was strongly asserted that when the light was central the arms would be level.

Abstractly three things can happen: (1) the kinaesthetic and postural impulses may be dominant; (2) the visual impressions may lead; (3) some kind of compromise solution may be effected.

The experimental results were as follows:

| Type of instruction | Percentage whose reaction was dominantly | | |
|---|---|---|---|
| | kinaesthetic | visual | compromise |
| Neutral | 54 | 17 | 29 |
| Tentative visual | 36 | 48 | 16 |
| Definite visual | 11 | 74 | 15 |

Two conclusions seem justified: first, facts of a non-sensory order can markedly affect sensorial reactions, and secondly, different individuals have a preferential bias towards particular types of sensorial reaction which may continue to operate even when special care is taken to abolish it. Within what limits these "other conditions" operate, and under what conditions preferential sensorial bias continues to act, are matters for further and urgently needed research.

A related but different problem of the same type has lately become of very great practical importance. There are many forms of instrumental operation in which a visual display is made the signal for a manipulatory adjustment, which then itself changes the display, calling for further muscular work, and so on. Very often the visual display does not keep perfect step with the objective changes which it is designed to record. The operator sees a change in the display which, however, appears to fall short of the objective adjustment that the situation demands. He thereupon alters the controls again, and this soon swings the visual change beyond its desired limits. Thus are set up a series of extremely undesirable oscillatory control movements. The case is complicated by the fact that every time a bodily movement is made, kinaesthetic and, ultimately, postural impulses are set up whose time-lag of appreciation differs from the visual. It will be seen at once that this kind of situation can be efficiently tackled only by completing a learning process in which either the "natural" differences of time-lag are allowed for, or in which the operator succeeds in interpreting changes of display and changes of control in such a way that they are treated as directly proportional one to another or as related in some constant manner. A learning

process, especially if it requires correction of what may be called "natural" tendencies, always remains, however, to some extent unstable, and is also liable to revert to the "natural" style when fatigue is produced. A better method may be to use some form of aided display, or aided control, to produce that combination of sensory cues which will involve the least possible amount of learning. What principles can, and should, be used to guide this are, however, at present almost entirely unknown.

Again, as everybody knows, some of the striking advances of recent physical knowledge have made it possible, to a degree formerly undreamed of, to achieve a visual representation of many auditory events. But when is it practically worth while to do this? Many people answer "always". The fact appears to be that when the visual representation exceeds a certain degree of complexity and rapidity of change, the eyes become less accurate in resolving or recognizing the event than the ears. It is then usually concluded that we should stick to the direct auditory signals alone. This is not the only possibility. When does a double representation in sensory terms confuse and when does it confirm decisive action? Nobody knows.

There are, in fact, a host of problems all of which at bottom have to do with the principles and laws of the conflict and confluence of different sensory modes. They are, almost always, questions calling for close co-operation between physics and psychology. I repeat that their solution will, in my opinion, constitute the next great step in the advance of knowledge in this field of the special senses.

## § 4. VISUAL PERCEPTION IN GENERAL

My first group of problems concerned the mode and conditions of operation of certain visual functions considered by themselves. My second group had to do with the effects of relating visual functions with those of other sensory modes which are contemporaneously excited. Neither alone nor together do these cover the whole field. All the senses, and particularly vision, have their complex setting of central nervous process. It is in the laboratory only that people live in a world of lights and shades, of tones, tastes, smells and specific bodily movements. Outside, their world is one of things and objects, and of movements the significance of which lies not in themselves, but in the aims which they serve. And these are all given a position in space and in time. The realistic problems are perceptual and not, except by analysis, sensory.

Recent years have added a great amount to our knowledge of the nature and determination of visual perception in almost all of its aspects. Yet rather surprisingly little of this has proved directly applicable to current problems of a practical kind. It is scarcely too much to say that the more elementary and fundamental the problem the less can its solution be stated with any certainty. I can do no more now than pick out one of these for illustration.

What is the precise relation between the measure of sensory—in our case of visual—acuity and any accredited measure or assessment of perceptual efficiency? In many directions—for the spotter who scans the sky for the approaching aircraft, for the look-out on a ship, for the inspector searching for faults in industrial production, often for the scientist watching the results of his

experiments—this is a question of great moment. Yet only partial and very scrappy answers can be given.

For many obvious reasons we are living at a time in which the process of dark adaptation has become one of vital practical significance. In the majority of cases when dark adaptation is needed, the eyes must not only react to the specific stimuli that are present, but the observer must locate and, within limits, identify the source of these stimuli. This happens to be an instance in which a careful experimental enquiry has been made, and it appears certain that a person's ability to perceive fairly complicated material is "determined only partially by the absolute threshold in cone vision; and still less by the absolute threshold in rod vision" (Craik and Vernon, 1942). That is to say, it is possible for all the peripheral retinal mechanism to reach a high degree of efficiency, and at the same time to find that when these mechanisms have to work in their full setting of central nervous functions, the result is disappointing and inaccurate. Conversely it is possible for the retinal factors involved to be below normal in efficiency, and still for the full machinery of visual perception to work accurately and well.

We can, however, go beyond this, and when we do we are confronted by facts which lead to hypotheses of a very wide-ranging character. It seems that the other conditions upon which effective visual perception depends are, speaking broadly, intelligence, education and temperamental bias. Caution and timidity stop a man from guessing; recklessness and suggestibility set him guessing wildly. Beyond doubt temperamental qualities of various kinds exercise a great influence upon visual perception. But nothing is yet known about this influence except in very general terms, and methods for its study are only just beginning to be shaped. Perhaps the position should be different as regards intelligence and education, for these have been the subjects of prolonged research.

When a form-perception test is tried under conditions of low illumination and it is found that the results fail to agree with the more radical brightness-difference test, the comment is always made that the reason for the disagreement is that the former demands intelligence and the latter only a good dark-adapted eye. It is therefore interesting that when an attempt was made to correlate the degree of efficiency of visual perception with the level of intelligence as indicated by intelligence tests of proved credit, no positive result whatever was secured.

Now intelligence is a subject of several very stubborn conventions. These vary from one social group to another, but within any such group they are astonishingly strong and persistent. It was probably a very sound impulse which led another great English scientist, Hughlings Jackson, to connect intelligence with "formulation", the process by which materials presented to the senses are analysed, combined, and the results expressed in some system of signs, like words or numbers, so that they can be permanently utilized by anybody. This notion, derived from one source or another, has certainly had an extraordinary influence, both upon education and upon the design of widely-accredited tests of intelligence. We know now, however, that a high degree of

facility in the use of one kind of sign-system does not necessarily carry with it a high degree of facility in the use of another. And the fact that intelligence as rated by the solution of problems set in terms of words, numbers and the relations of conventionalized shapes has no significant positive relationship to at least one form of efficiency in visual perception suggests that perhaps there is an intelligence which has nothing to do with any system of signs. This, it may be, is the basic intelligence of the expert clinician, of the artist, of the cultured appreciation of arrangements of lights, colours, shapes and tones, of the epicure, and, particularly important in this mechanical age, of the craftsman. Then it is not surprising to find that, say, the expert in visual perception, called upon to express his particular *expertise* in some other medium, may be ranked as of lowly intelligence.

If this expertness of the eye, the muscles, the ear, delicately sensitive to the character and arrangement of its sensory materials, yet not going beyond direct appreciation and manipulation, is worthy to be called intelligence, it is somewhat disturbing to meet more and more decisive claims that man's whole station in life should be settled by his rank in the use of the particular system of signs which are constituted by words, numbers and highly conventionalized shapes. It is equally disturbing to find the great bulk of formal education shaped by the same demand.

I believe it correct to speak of a visual "intelligence". I believe it consonant with the wide use of this term in daily life. Even if we do not accept the wider implications of this at which I have hinted, there is one consequence from which we cannot escape. We may compare two ways of ranking or assessing functions which are purely or predominantly retinal and find that they disagree. We may then say, as many have in like circumstances, that because one way has to deal with more complex materials than the other, it is more saturated with intelligence. If we do, we must see that the test of that hypothesis is suited to the occasion, and is limited to the rapid and accurate appreciation and direct manipulation of materials proper to the sense of vision. Only if we do this can we begin to tell precisely how the simpler measures of visual acuity and eye-muscle control, and how the interaction of the visual with the other senses, are related to the full phenomena of visual perception.

## § 5. CONCLUSION

In this lecture I have picked out and exemplified three levels of current visual problems. The first concerns the predominantly peripheral mechanism of the single sense. The second deals with largely unknown effects of the concurrent excitation of the visual and other sensorial functions. The third takes up the relation of both of these to visual perception, with its full setting of complex central activity.

I wonder what a re-incarnated Thomas Young would think of it all. I fancy that he might rather like the first as being in direct succession to the pre-occupation of his youth; that he might tolerate the second, but that he would have little use for the third. He himself ran easily to words—clear, precise and scientifically arranged—but he had little appreciation for the intelligence which cannot and does not wish to be communicated. He would well have understood that the mute Milton must be inglorious, but I think it would never have occurred

to him to rank the villager, withstanding "the petty tyrant of the fields", as a Hampden.

There is, however, a wider sense in which my remarks might prove wholly acceptable to him. Like many another, Young was violently attacked in the *Edinburgh Review*. He replied, and in the course of one of his replies laid down what he took to be the principles of scientific method. There are two sorts of scientific investigation: "the one analytical, where we proceed from the examination of effects to the investigation of causes; the other synthetical, where we first lay down the causes, and deduce from them the particular effects".

It is curious and very interesting that his first steps in scientific discovery were taken partly along the analytical path. He observed, as minutely as he could with the methods available at the time, the actual effects upon the curvature of the lens of focusing the eye upon near and more distant objects, and rested his explanatory mechanism largely upon this. But as he went on his own method became more and more exclusively synthetical. This he well knew, and with great honesty set forth its limitations:—

"We necessarily begin by assuming principles which ought, in such a case, to bear the modest name of hypothesis; and when we have compared their consequences with all the phenomena, and have shewn that the argument is perfect, we may justly change the temporary term *hypothesis* into *theory*. This mode of reasoning is sufficient to attach a value and importance to our theory, but it is not fully decisive with regard to its exclusive truth, since it has not been proved that no other hypothesis will agree with the facts".

Looking back upon the full story of his work he says, half regretfully, that after all there may be other hypotheses.

Nowadays the range, delicacy and accuracy of factual observation have been immeasurably increased. With all those current problems of visual function and visual perception I have mentioned, and with many others that I might have brought forward, there are, as I have indicated, the leading, the "synthetical" ideas which must guide observation. Then there is no way but this: the examination of effects, whenever possible by experiment, which will show their consonance with the one hypothesis only. Whatever he might think about my topics, with this union of synthesis and analysis I am sure that Thomas Young would be well content.

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# NEWTON'S VERSES*

By E. N. da C. ANDRADE, F.R.S.

*MS. received* 15 *March* 1943

WRITERS on Newton's life—Brewster, L. T. More and J. W. N. Sullivan, among others—quote the following verses as having been written by Newton beneath a picture of Charles I which he drew:

" A secret art my soul requires to try,
If prayers can give me, what the wars deny.
Three crowns distinguish'd here in order do
Present their objects to my knowing view.
Earth's crown, thus at my feet, I can disdain,
Which heavy is, and, at the best, but vain.
But now a crown of thorns I gladly greet,
Sharp is the crown, but not so sharp as sweet,
The crown of glory that I yonder see
Is full of bliss and of eternity."

Our authority for these verses is Stukeley, who says that Mrs. Vincent, " of this town " (Grantham), repeated them to him, by memory. Stukeley adds that, " She fancyed, and aver'd it that he composed them himself. I rather suppose he copyed the print prefixed to the *Eikon basilice* ". Nevertheless, the authorities quoted above all speak of them as if they were original, and More even says: " These are very good verses in the fashion of the day to be written by a boy of his age, and I accept his † statement of his skill, as I believe he could excel in any undertaking to which he applied his mind or hands ".

To show that the lines are undoubtedly taken from the *Eikon basilice* I append the verses that there appear:

" The Explanation of the Frontispiece

A sacred heat inspires my Soul to trie
If *Pray'rs can give Me what the Warres denie,*
Three Crowns distinctly here in order do
Present their objects to my knowing view,
*Earth's Crown lies humbled at my foot, disdain,*
*'Twas bright, but heavie, and withall but vain,*
*And now by Grace a Crown of Thorns I greet,*
*Sharp was this Crown, but not so sharp as sweet* :
This was Christ's crown, my book upon my bord
Explains my heart, *My hope is in thy Word.*
My starrie Crown of Glorie, last I see,
*As full of Blisse, as of Eternitie.*
Now look behind, and midst most troubled skies
Behold, how *clearer I from darknesse rise,*
And stand *unmov'd triumphant,* like a Rock,
'Gainst all the waves, & winds tempestuous shock,
So like the Palm, which heaviest weights do trie,
*Virtue opprest, doth grow more straight and high.*"

* A note to the lecture on " Newton " (*Proc. Phys. Soc.* **129** (1943)).

† Apparently Stukeley's, although I cannot find any statement of Stukeley's that Newton was skilled in making verses, though he says that he was expert with his pen, which, from the context, clearly refers to his drawings.

There seems not the slightest doubt that the verses written by Newton are the above imperfectly recollected, with lines 9 and 10 and the last six lines omitted. Mrs. Vincent may well have forgotten the couplet 9 and 10, and Newton probably had no room for the last lines. Mrs. Vincent was probably not very accurate, especially since, as pointed out by Mr. White, editor of Stukeley, the version quoted by Brewster differs verbally from that in the printed Stukeley, quoted above. The picture of Charles I which Newton made to go with the verses was, no doubt, a copy of the frontispiece to the *Eikon basilice*.

The verses are, then, merely another example of Newton's habit of copying out passages from books. I have already * pointed out that all the rules for drawing and making colours which appear in Newton's youthful notebook, together with sundry other receipts, to the number of some seventy in all, and which were printed by Professor David Eugene Smith, were copied literally from Bate's *Mysteryes of Nature and Art*. This habit of copying persisted. The *Catalogue of the Portsmouth Collection* lists five parcels containing transcripts from various alchemical authors, in Newton's handwriting, comprising nearly 150 items in all, and Lord Keynes informs me that he possesses a number of other transcriptions from authors.

There is, then, as far as I know, nothing extant to support the statement said to have been made by Newton to Conduitt, that he had, when young, "excelled particularly in making verses".† He probably referred to schoolboy doggerel, for in later life he often expressed a contempt for poetry, and among his books listed by Villamil there is not one of the English poets. Lord Radnor records that in answer to a friend who asked his opinion of poetry, Sir Isaac replied: "I'll tell you that of Barrow; he said that poetry was a kind of ingenious nonsense".‡ The *Eikon basilice* verses, though poor and conventional, show some slight feeling for poetry. I do not think that Newton can ever have written anything even as good as this.

* *Nature*, **135**, 360 (1935).
† Brewster, vol. i, p. 12.
‡ Spence's *Anecdotes*.

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# A NOTE ON A COMPENSATED HOT-WIRE AIR THERMOMETER

By M. A. EL-SHERBINI and Y. L. YOUSEF,
Fouad I University, Cairo

*MS. received* 26 *May* 1943

A very simple model of a compensated hot-wire air thermometer for measuring currents at frequencies up to radio-frequencies can be easily constructed from a thermally screened (cotton-packed) differential micromanometer of the Roberts type, fitted with a hot wire in each limb. The manometric liquid is paraffin oil, enclosing in the measuring capillary tube an air bubble of which the length is approximately equal to the distance between

the centres of the two limbs. The instrument is by this means made practically indifferent to changes of level. The method of filling and adjusting the position and the length of the index bubble is a matter easily learned by experience. If care is taken to exclude substances of high vapour pressure, the natural creep of the zero, which is common in appliances of this class, becomes negligibly small.

With a platinum wire 4 cm. in length, 0·0025 cm. in diameter, and 8·5 ohms in resistance, in a cylindrical bulb of 30 ml. capacity, 3 cm. in diameter, connected to the (similar) compensating bulb by 0·86 mm. capillary, the sensitivity is 0·5 mm. per $10^{-4}$ watt, which is of the same order of magnitude as that reported by Scheibe (1925). The sensitivity is increased by reducing the diameter of the capillary. The readings are consistent to less than 5%, and the time before a steady state is reached is less than 1 minute. The ultimate displacement of the index is merely proportional to the quantity of energy absorbed.

The measurements may be conducted by a null method if a compensating current is applied to the other wire. This is particularly valuable when dealing with large quantities of energy. Calibration is carried out with direct current. The test current $I_0$ is determined by means of the current $I_1$, which, when passed in the same wire, produces the same displacement (or, in the null method, requires the same compensating current $I_2$ in the second wire). The bubble does not change in length, as it does with instruments using a liquid thread.

REFERENCE

SCHEIBE, A., 1925. *Jb. drahtl. Telegr.* **25**, 12.

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# A NOTE ON A SIMPLE BARETTER

BY M. A. EL-SHERBINI AND Y. L. YOUSEF,
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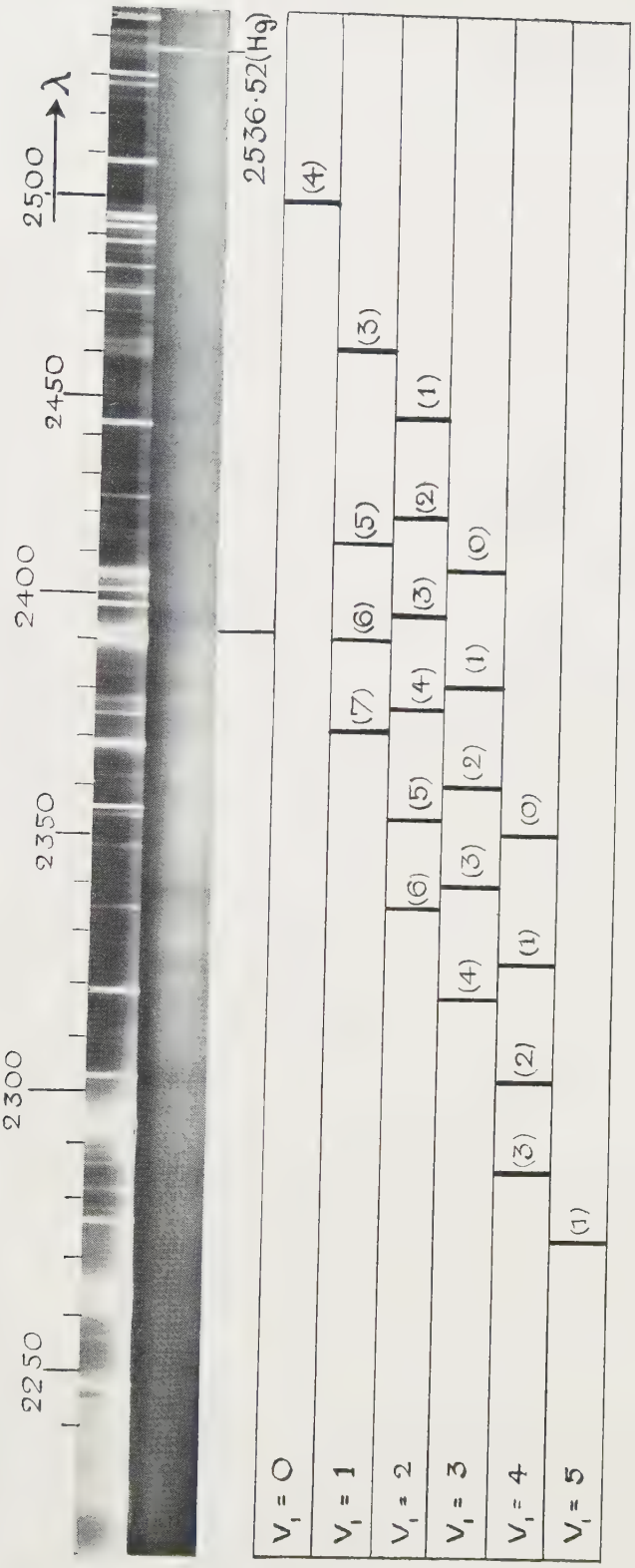
*Abstract received* 6 *August* 1943, *the MS. of the paper having earlier been lost in transit*

*ABSTRACT.* A simple baretter can be readily made from four commercial torch-lamps (3·5 volts) whose filaments are twisted in the form of the letter S. The lamps are first sensitized by careful ageing for a few hours at the maximum current, which is about 250 ma. (passed interruptedly), until the normal resistance (1·3 ohms) is nearly trebled. They are then arranged in a square mesh in which two opposite corners are connected to the test supply, while the other two are joined to the measuring circuit. The latter may be either a constant-current bridge, or a low-resistance potentiometric arrangement. The polarizing current has an optimum value, which can be found by trial. If the arms of the baretter unit do not happen to have equal resistances at the optimum working current, or at least do not satisfy among themselves the Wheatstone-bridge relation, a short length of a fine external wire of appropriate resistance may be added to the smallest arm.

With lamps having a resistance of 3·2 ohms when traversed by a polarizing current of 70 ma., and with a wire potentiometer joined to the polarizing ends and containing as a balance indicator a pointer galvanometer having a resistance of 100 ohms and a sensitivity of 1/4 $\mu$a. per scale division, the want of balance produced by the change of baretter




Absorption spectrum of formic acid, with copper for comparison.
(Integers in brackets are $v_2$ values.)

*To face page 428*

Formic acid absorption bands observed between 2500 A. and 2260 A.

| $\lambda$ (A.) | Intensity | $\nu$ (cm.$^{-1}$) | $v_1$ | $v_2$ |
|---|---|---|---|---|
| 2499·96 | 1 | 39989 | 0 | 4 |
| 2461·15 | 4 | 40619 | 1 | 3 |
| 2443·4 | 4 | 40914 | 2 | 1 |
| 2420·8 | 6 | 41296 | 2 | 2 |
| 2414·3 | 4 | 41407 | 1 | 5 |
| 2408·4 | 4 | 41509 | 3 | 0 |
| 2398·3 | 10 | 41684 | 2 | 3 |
| 2394·7 | 5 | 41746 | – | – |
| 2391·2 | 4 | 41810 | 1 | 6 |
| 2382·2 | 9 | 41958 | 3 | 1 |
| 2377·16 | 6 | 42054 | 2 | 4 |
| 2372·8 | 5 | 42131 | 1 | 7 |
| 2361·5 | 9 | 42334 | 3 | 2 |
| 2354·0 | 6 | 42469 | 2 | 5 |
| 2350·7 | 3 | 42528 | 4 | 0 |
| 2340·3 | 10 | 42717 | 3 | 3 |
| 2335·8 | 6 | 42799 | 2 | 6 |
| 2325·2 | 9 | 42994 | 4 | 1 |
| 2318·9 | 7 | 43111 | 3 | 4 |
| 2302·9 | 8 | 43411 | 4 | 2 |
| 2284·9 | 10 | 43752 | 4 | 3 |
| 2273·3 | 5 | 43975 | 5 | 1 |

Errors in $\nu$ (cm.$^{-1}$)

| $v_1$ \ $v_2$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| 5 | +38 | | | | | | |
| 4 | −14 | −46 | −2 | | | | |
| 3 | −11 | −2 | 0 | −9 | | | |
| 2 | 0 | +3 | 0 | +15 | −15 | +40 | |
| 1 | | | +32 | | +14 | −4 | +60 |
| 0 | | | | +14 | | | |

resistance due to the passage of a test current of 5 ma. (40 cycles/sec.) is 55 scale divisions. The time for the ultimate deflection is 30 seconds. The alternating-current watt consumption per scale division is about $10^{-1}$. This is of the same order of magnitude as the watt sensitivity in the bolometer constructed by Gati (1909).

The safety factor is large, and the range can be easily extended up to 250 ma. by simply calibrating against the displacement of the balance point of the potentiometer wire.

REFERENCE

GATI, B., 1909. *Phys. Z.* **10**, 897.

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# THE ULTRA-VIOLET ABSORPTION SPECTRUM OF FORMIC ACID

BY B. SUGARMAN,
Imperial College

*MS. received* 19 *June* 1943

*ABSTRACT.* The absorption bands of formic acid at room temperature between 2260 and 2600 A. have been observed and found to follow the formula

$$1/\lambda = 37754 + 1033(v_1 + \tfrac{1}{2}) + 385(v_2 + \tfrac{1}{2}).$$

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At temperatures from 0° C. to 140° C., formic acid exhibits strong ultra-violet absorption bands within the range 2600 A. to 2260 A. This absorption has been investigated with a Hilger medium quartz spectrograph and Ilford Q1 plates, at various temperatures between 0° C. and 25° C., the corresponding saturation vapour pressures varying from 11·2 mm. to 44 mm. A path length of 85 cm. was used throughout, with a hydrogen discharge tube as source.

For exposures of not less than 1 minute, formic acid shows diffuse bands which apparently have no definite heads; the most intense of these bands appear at 2398·3, 2382·6, 2361·5, 2340·3, 2325·2, 2302·9 and 2284·9 A. (see plate).

The wave-lengths of the visual centres of the bands were measured with an accuracy of $\pm 0{\cdot}5$ A. for the more intense and $\pm 1{\cdot}0$ A. for the less intense.

Below 2260 A. absorption is continuous at least as far as 1900 A.

The wave-lengths of the majority of the bands observed in this investigation may be represented approximately by the formula

$$1/\lambda \text{ cm.} = 37754 + 1033(v_1 + \tfrac{1}{2}) + 385(v_2 + \tfrac{1}{2}),$$

where $v_1$ and $v_2$ have values as indicated in the plate and table. Since this formula does not contain the terms in $w(v+\frac{1}{2})^2$ which occur in the general formula, it is to be expected that the formula given here will only approximately represent the bands.

The maximum errors (approximately 3·0 A.) in calculating the wave-lengths from this formula are associated with the weaker bands. The errors in $\nu(\text{cm.}^{-1})$ in using the formula are shown in the second table opposite.

The null band for which $v_1 = 0$ and $v_2 = 0$, as calculated from the formula, corresponds to $1/\lambda = 38463$ cm.$^{-1}$, i.e. $\lambda = 2598{\cdot}9$ A.

Harris (1926) has previously detected ultra-violet absorption bands of formic acid and represented them by $1/\lambda = 41700 + 1050n + 385p$, where $n$ and $p$ are integers varying from $-2$ to $+2$ and $-7$ to $+7$ respectively.

Since my investigation was carried out at low temperatures, the frequency differences of the observed bands are mainly upper-state separations; however, at high temperatures the probability of transition from the different levels of the lower state is increased and, as Harris suggests, his value of 1050, or my value of 1033, may be attributed to the fundamental C—O vibration. An infra-red investigation of formic acid reveals an absorption band at $9{\cdot}15\,\mu$ (1093 cm.$^{-1}$), which supports this hypothesis.

ACKNOWLEDGEMENTS

I should like to thank Dr. R. W. B. Pearse and Professor H. Dingle for their help in the production of this paper.

REFERENCE

HARRIS, L., 1926. *Nature, Lond.*, **118**, 482.

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# REVIEWS OF BOOKS

*Elementary Physical Chemistry*, by MERLE RANDALL and LEONA ESTHER YOUNG. Pp. xiv + 455. (Berkeley, California: Randall and Sons, 1942.) $4.50.

Of the two authors of this book, one is well known for his work on thermodynamics, and the other is a " pure " chemist. Both have experience in teaching, and it is apparent from the volume now under review that neither is afraid of unconventional methods. The result is a stimulating treatment, which gains a further effect of novelty by being reproduced from typescript.

The book opens with an introduction to the modern concept of matter, and figure 1 on page 1 shows the electron cloud in the $2\,^2S_{\frac{1}{2}}$ state of a hydrogen-like atom, though the precise meaning of this description must be sought elsewhere by any student who wishes to have an exact knowledge. It then goes on to vaporization, solutions, gases, thermochemistry and electrolysis, with particularly interesting chapters *en route* dealing with indicators and buffer solutions, and with fluid friction.

On the whole, the main impression left on the reader is the extent to which the profession of chemical engineering has reacted on the teaching of this subject, at any rate in the case of these writers. Quite early, the student is encouraged to draw up flow sheets, and in many other ways the point of view of the large-scale worker is clearly seen to be operative in deciding the treatment.

The book is one to be recommended to those who teach this subject, even if they do not wish to adopt it as a text-book; it contains many suggestions which could usefully be introduced into other, more academic, courses. J. H. A.

*The Cathode Ray Oscillograph in Industry*, by W. WILSON. Pp. xxi + 150, 156 figures. (London: Chapman and Hall, Ltd.) 12*s*. 6*d*. net.

The importance of the cathode-ray oscillograph as an instrument both for research and for industrial control is well recognized, but further uses are still to be developed. The appearance, therefore, of a book giving an account of some of the numerous uses to which this tool can be put is very welcome. Some idea of the field covered by Dr. Wilson may be obtained by noting that figure 1 bears the legend " Sir J. J. Thomson's cathode-ray

tube ", while figure 148 is a reproduction of an electron micrograph of tobacco mosaic virus at a magnification of 55,000. Where so long a road is travelled, descriptions are necessarily brief, but on the whole these are clear and well arranged.

The book begins with four chapters devoted to the description of various component parts of the cathode-ray oscillograph and the accessory circuits necessary for its use for the measurement and recording of transient phenomena. Both the continuously evacuated metal type and the sealed-off glass tubes are adequately described and illustrated.

Chapters V to X contain accounts of a variety of uses to which cathode-ray oscillographs have been put. Dr. Wilson classifies these in order of increasing complexity ; he starts with tests requiring the use of but a single pair of deflectors, and here we find, among other interesting applications, a description of a continuous thickness-indicator for gauging the quality of a strip of metal as it comes off the rolls. In chapter VI the second pair of deflecting plates is brought into use, and examples include phase-difference measurements and direction finding. The following chapter deals with tests requiring a repeating time-base ; both cyclic and recurrent surge-phenomena are treated. The more exacting conditions met with in investigating transient phenomena which do not recur receive attention in chapter VIII, and here we find examples ranging from recordings of lightning surges to the use of the electro-cardiograph. The next two chapters are devoted to tests involving independent bases other than time : one of them is wholly concerned with the recording of mechanical pressures.

Dr. Wilson has a surprise in store for us in his eleventh chapter, entitled *The Electron Microscope*. He here describes electron lenses, the Finch electron-diffraction camera and both the Metropolitan Vickers' and the Radio Corporation of America's electron microscopes. The book ends on a practical note with a chapter giving advice on construction, operation and maintenance of equipment.

Within the limitations he has set himself, Dr. Wilson has produced a satisfactory book which can safely be recommended. The quality of the diagrams and of the numerous plates is excellent. G. D. P.

*Prism and Lens Making*, by F. TWYMAN, F.R.S. Pp. iv + 178. (London: Adam Hilger, Ltd., 1943.) 15*s*.

The art or " mystery " of optical working has until recent times been regarded as a professional secret of which only the most vague descriptions were readily available in books ; and, indeed, there is a sense in which no text-book description, however excellent, can do more than partially lighten the difficulties of mastering such a subject and acquiring the technical skill for producing good lenses. But the irrepressible amateur astronomers who learned under the benevolent guidance of the Rev. Mr. Ellison to make their own reflecting telescopes found the " mystery " to be a fascinating hobby, and a number of books intended for amateur and technical use have appeared, amongst them being those of Orford, Dévé and Wright, and the symposia issued by the *Scientific American*. Physicists also have discovered that simple optical parts can be made in the laboratory without the delay incurred in obtaining professional help. But even now the appearance of this book, written by the managing director of a firm with such a deservedly high reputation as that of Messrs. Adam Hilger, Ltd., is something of a portent, and seems to mark the passage of optical work from a " mystery " into a well-documented branch of engineering production. It is the kind of work which would be of great value to an apprentice entering such a firm, and it describes the modern type of practice, including special adaptations of modern milling and grinding machines for the pre-formation of lenses and prisms. The methods used in this connection differ greatly, of course, between various optical factories, whereas (as the author remarks) there are many features of the fine grinding and polishing process which have remained static for hundreds of years. But Mr. Twyman has not been content to leave the details, such as the hardness of pitch, balsam, etc., to the casual methods of the past, for a more scientific control has been established at every possible point. Technicians will find of especial interest the details of the single-surface machine for working flat surfaces to high accuracy, and valuable hints will be picked up in the chapter on making and working blocks of prisms, though it is in such connections that the inevitable gap between the written word and the handling

of the job will probably be widest for the beginner. One feature which will be much appreciated is the useful information on various materials and their sources of supply.

It is natural to find that in the chapter on testing, the chief emphasis is placed on the Twyman-Green interferometer ; and some useful hints are given on the use of this instrument for precision testing of prism angles. The general claim is (to quote from the preface) " these methods and machines will enable even an unskilled worker, after a short period of training under competent supervision, to produce work of the first quality as far as definition and accuracy of angle are concerned ". It will be gladly admitted that Mr. Twyman and his colleagues can, in fact, " deliver the goods ".

The author hints in the preface that there may be other and better methods in use in different establishments, and suggests that if descriptions of such methods could be collected a " reliable and complete text " might become available. It will be correctly inferred that the present volume does not aim at completeness or even a systematic presentation of the subject in the sense attempted by Dévé ; in fact the inclusion of a vocabulary of French technical-optical names and phrases seems to hint that the latter author should be consulted for additional information. The book does not include, for example, any systematic theory of the grinding process or details of the correction of faults in the polishing of large surfaces. Moreover, the description of testing methods is confined to those which have found most favour in the Hilger workshops. The description of the use of the " Angle Dekkor " in conjunction with surface-plate and steel blocks with standard angles does not hint at other quite effective ways of testing prism angles with an auto-collimator.

The section on the star test is mainly limited to a quotation and illustration from the late Mr. H. Dennis Taylor's *Adjustment and Testing of Telescope Objectives*, written long before any exact calculations or other investigations of the distribution of light in the star disk (as afflicted with aberrations) had been made ; and the appearances pictured in this plate illustration might with advantage have been revised in some details (for example, the star disks attributed to " squaring-on " error and astigmatism).

Other tests (Foucault, Ronchi, etc.) are dismissed with no more than a mention, though it must be admitted that many discerning workers with the necessary experience have found them extraordinarily useful in many cases where interferometry is not possible —for example, in the earlier stages of forming lenses with aspheric surfaces ; and the apparatus is, needless to say, very much less expensive. Does the textual reference to a test due to " Birch " refer to the work of Dr. C. R. Burch in developing the phase-contrast methods due to Professor Zernike.*

In spite of such omissions as have been mentioned, Mr. Twyman has performed a most useful service with this volume, and has contributed greatly to the possibility of effectively educating optical workers to take an intelligent and enlightened interest in this task. The only thing that the present reviewer would beg leave to doubt is whether this brilliantly written but very individual book should (at the present stage) have been described as a " text-book ". In some senses it undoubtedly is such ; but when the ideal text-book comes to be written we hope it will reflect a more catholic view of the subject.

L. C.

* Burch, *Monthly Notices R.A.S.* **94,** 384 (1934) ; Zernike, *ibid.* **94,** 377 (1934).

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## CORRIGENDUM

E. F. Herroun. *Proceedings*, this volume, part 4 (1 July 1943) :

p. 342, second line. *For* 2·38 *read* 23·8.

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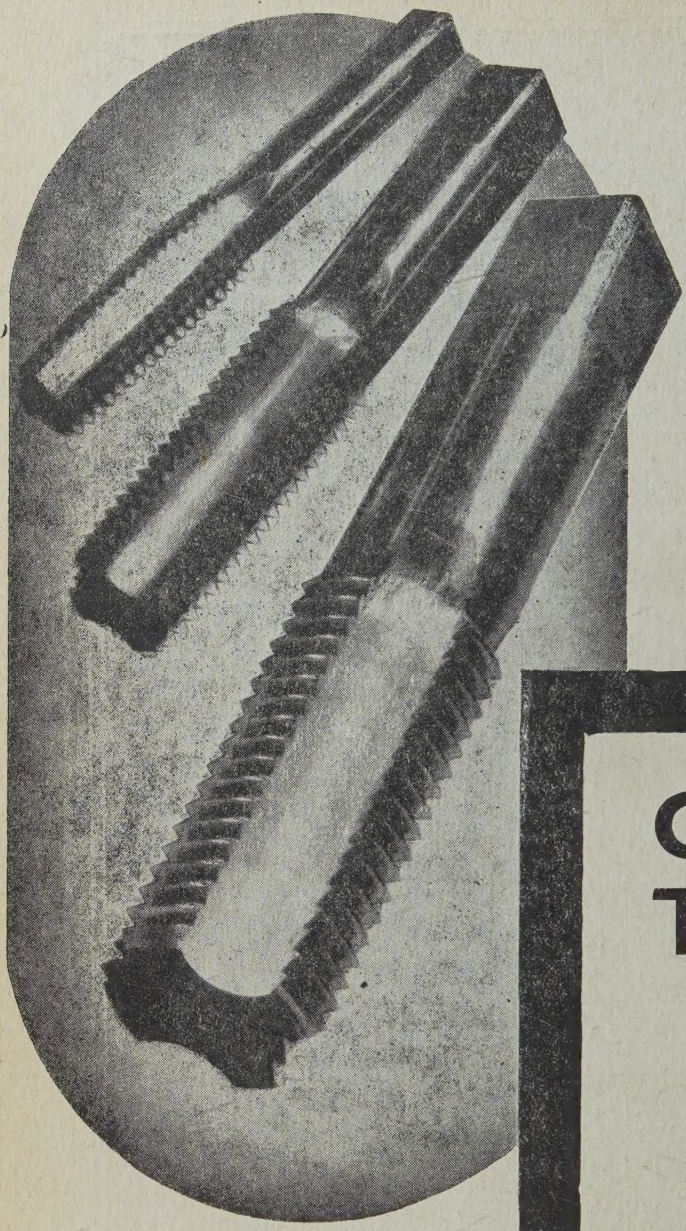

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